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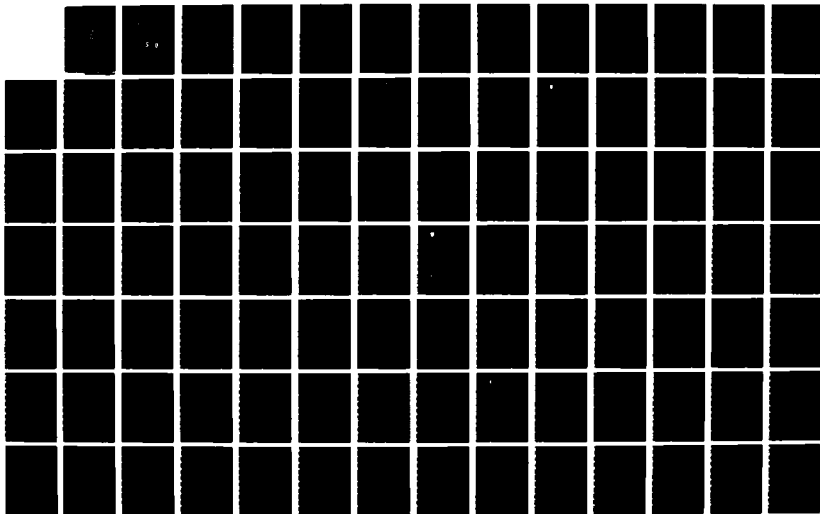
INTERNATIONAL CONFERENCE ON CHEMICAL KINETICS PROGRAM  
AND ABSTRACTS HELD (U) NATIONAL BUREAU OF STANDARDS  
GAITHERSBURG MD NATIONAL MEASURE J T HERRON ET AL

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**INTERNATIONAL CONFERENCE  
ON CHEMICAL KINETICS**

AFOSR-TR- 87-0707

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**PROGRAM AND ABSTRACTS**

JUNE 17-19, 1985  
NATIONAL BUREAU OF STANDARDS  
GAITHERSBURG, MARYLAND, U.S.A.

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National Science Foundation

87 6 5 091

4. PERFORMING ORGANIZATION REPORT NUMBER(S)			5. MONITORING ORGANIZATION REPORT NUMBER(S)  <b>AFOSR-TB- 87-0707</b>		
6a. NAME OF PERFORMING ORGANIZATION National Bureau of Standards		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION AFOSR		
6c. ADDRESS (City, State, and ZIP Code) National Measurement Lab Gaithersburg, MD 20899		7b. ADDRESS (City, State, and ZIP Code) Building 410 Bolling AFB DC 20332-6448			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR		8b. OFFICE SYMBOL (If applicable) NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR-ISSA-85-0062		
8c. ADDRESS (City, State, and ZIP Code) Building 410 Bolling AFB DC 20332-6448		10. SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO 61102F	PROJECT NO 2303	TASK NO B1	WORK UNIT ACCESSION NO
11. TITLE (Include Security Classification) INTERNATIONAL CONFERENCE ON CHEMICAL KINETICS (U)					
12. PERSONAL AUTHOR(S) John Herron, Chairman; Wing Tsang, Stephen E. Stein, David M. Golden					
13a. TYPE OF REPORT FINAL		13b. TIME COVERED FROM 85/03/15 TO 85/09/30		14. DATE OF REPORT (Year, Month, Day) 1985 June	
15. PAGE COUNT 184					
16. SUPPLEMENTARY NOTATION Printed by the National Bureau of Standards, Gaithersburg, MD, June 1985					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	kinetics, reactions, energy transfer		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)  This meeting held at the National bureau of Standards, Gaithersburg, MD, brought together leading investigators from universities, research laboratories, and industrial organizations to review the progress and problems in theoretical and experimental chemical kinetics. The scope of the meeting was broadened to include ion-molecule reactions and processes occurring in the condensed phase. Other topics covered unimolecular and bimolecular reactions, energy transfer, and a symposium in honor of Professor Sidney W. Benson.					
20. DISTRIBUTION AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS PPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr Francis J. Wodarczyk			22b. TELEPHONE (Include Area Code) (202) 767-4963		22. OFFICE SYMBOL AFOSR/NC

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Accession For	
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DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
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Date Recd.	
Availability Code	
Distribution Statement	
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## Preface

The purpose of this meeting is to bring together leading investigators from universities, research laboratories and industrial organizations to review the progress and problems in theoretical and experimental chemical kinetics. It is in many ways a continuation of the highly successful symposium held at the National Bureau of Standards seven years ago under the chairmanship of Professor Frederick Kaufman, entitled "Current Status of Kinetics of Elementary Gas Reactions: Predictive Power of Theory and Accuracy of Measurement." Since that meeting much progress has occurred in terms of measurement and theory. Recognition of the unifying features of chemical change has been particularly impressive. Hence, the scope of the meeting has been broadened to include ion-molecule reactions as well as processes occurring in the condensed phase. It is hoped that by bringing together many of the outstanding workers in this field it will be possible to re-evaluate the foundation of chemical kinetics and point out critical directions for future endeavor. It is thus particularly appropriate that we take this occasion to honor Professor S. W. Benson for his seminal contributions in this area and particularly his vision of chemical kinetics as an integral part of chemical science.

## Table of Contents

	Page
PROGRAM. . . . .	1
POSTER PRESENTATIONS . . . . .	5
ABSTRACTS OF INVITED TALKS . . . . .	17
ABSTRACTS OF POSTER PRESENTATIONS	
Poster Session A. . . . .	43
Poster Session B. . . . .	72
Poster Session C. . . . .	104
Poster Session D. . . . .	125
Poster Session E. . . . .	145
AUTHOR INDEX . . . . .	182

**International Conference on Chemical Kinetics**

**June 17-19, 1985**

**Program**

**Sunday, June 16**

6:30-8:30 p.m. Registration and Reception, Quality Inn, Gaithersburg, MD

**Monday, June 17**

7:45 a.m. Buses leave hotels for NBS

8:00 a.m. Registration Begins

8:30 a.m. Greetings, John Herron

8:35 a.m. Welcome, Donald R. Johnson, Director  
National Measurement Laboratory  
National Bureau of Standards

8:45 a.m. Opening Remarks, David Golden

**First Session - In Honor of Sidney Benson**

**Chairman: R. Srinivasan**

9:15-9:45 a.m. "Kinetic and Product Studies of the Thermal Decomposition of Dimethylsilane in a Single Pulse Shock Tube and in a Stirred Flow Reactor"  
S. F. Rickborn, D. S. Rogers, M. A. Ring, and H. E. O'Neal

9:45-10:15 a.m. "Thermochemical Kinetics - A Success Story?"  
Robin Walsh

10:15-10:45 a.m. "Kinetics and Mechanism of the Thermal Decompositions of Unsaturated Aldehydes: Benzaldehyde, Crotonaldehyde and 2-Furaldehyde"  
M. A. Grela and A. J. Colussi

10:45-11:15 a.m. Coffee

11:15-11:45 a.m. "Hydrogen Transfer Between Polyaromatic Molecules"  
Stephen E. Stein

11:45-12:15 p.m. "Kinetics of Primary Processes in the Pyrolysis of Cyclopentanes and Cyclohexanes"  
Trevor C. Brown, Keith D. King and Tam T. Nguyen

12:15-12:45 p.m. "Some Kinetic and Thermochemical Aspects of Sodium in the Stratosphere"  
Sidney W. Benson and John J. Lamb

12:45-1:45 p.m. Lunch



## Second Session - Fundamentals

Chairman: Richard M. Noyes

- 1:45-2:15 p.m. "The  $F+H_2$  Potential Energy Surface. The Ecstasy and the Agony"  
Henry F. Schaefer III
- 2:15-2:45 p.m. "Elementary Reactions in Compressed Gases and Liquids: From Collisional Energy Transfer to Diffusion Control"  
J. Troe
- 2:45-3:15 p.m. "Comparison of Thermodynamics and Kinetics for Some Important Bond-Making and -Breaking Processes in Organic Chemistry"  
Edward M. Arnett
- 3:15-4:30 p.m. Coffee and Poster Session
- 4:30-5:30 p.m. Reconvene and Discussion

## Tuesday, June 18

- 8:15 a.m. Buses leave hotels for NBS

## Third Session - Unimolecular Reactions

Chairman: Michael Bowers

- 9:00-9:30 a.m. "Unimolecular and Intramolecular Dynamics. Relationship to Potential Energy Surface Properties"  
William L. Hase
- 9:30-10:00 a.m. "The Dissociation Dynamics of Energy Selected Ions"  
Tomas Baer
- 10:00-10:30 a.m. "Empirical Approach to Substituent Rate Effects in [3,3]-Sigmatropic Shifts Utilizing the Thermochemistry of Coupled Nonconcerted Alternative Paths. III"  
Joseph J. Gajewski and Kevin E. Gilbert
- 10:30-11:45 a.m. Coffee and Poster Session
- 11:45-12:45 p.m. Reconvene and Discussion
- 12:45-1:45 p.m. Lunch

## Fourth Session - Energy Transfer

Chairman: Simon H. Bauer

- 1:45-2:15 p.m. "Energy Transfer"  
H. Monty Frey

- 2:15-2:45 p.m. "Large Molecule Energy Transfer: New Techniques and New Controversies"  
John R. Barker
- 2:45-3:15 p.m. "Vibrational Relaxation of Chemical Bonds in Liquids and on Surfaces"  
John C. Stephenson
- 3:15-4:30 p.m. Coffee and Poster Session
- 4:30-5:30 p.m. Reconvene and Discussion
- 7:00-10:00 p.m. Reception/Banquet

**Wednesday, June 19**

- 8:15 a.m. Buses leave hotels for NBS

**Fifth Session - Reactions in the Liquid Phase**

**Chairman: Cheves Walling**

- 9:00-9:30 a.m. "Prediction of Rate Constants for Ionic Reactions in the Gas Phase and in Solution"  
John I. Brauman, James A. Dodd, and Chau-Chung Han
- 9:30-10:00 a.m. "Measurement of Absolute Propagation and Termination Rate Constants for Alkylperoxyls in Solution by the Hydroperoxide Method"  
J. H. B. Chenier and J. A. Howard
- 10:00-10:30 a.m. "Kinetics and Mechanisms of Inorganic Reactions in Aqueous Solutions: Intermediates"  
James H. Espenson
- 10:30-11:45 a.m. Coffee and Poster Session
- 11:45-12:45 p.m. Reconvene and Discussion
- 12:45-1:45 p.m. Lunch

**Sixth Session - Bimolecular Reactions**

**Chairman: Michael Pilling**

- 1:45-2:15 p.m. "Measurement and Understanding of Gas-Phase Bimolecular Reactions"  
F. Kaufman
- 2:15-2:45 p.m. "Theoretical Characterization and Calculation of Potential Energy Surfaces for Chemical Reactions"  
Thom. H. Dunning, Jr.
- 2:45-3:15 p.m. "Laser Stimulation and Observation of Bimolecular Reactions"  
J. Wolfrum

3:15-4:30 p.m. Coffee and Poster Session

4:30-5:30 p.m. Reconvene and Discussion

5:30 p.m. Adjourn

POSTER SESSION A

	<u>Page</u>
A-1 General Classical Variational Theory of the Rates of Atom-Diatom Reactions G. W. Koeppel and D. I. Sverdlik .....	44
A-2 Theoretical Study of the H + XY Reactions (X,Y = F-I) Robert A. Eades and Thom. H. Dunning, Jr.....	45
A-3 Theoretical Study of the Li + HF Reaction Robert A. Eades and Thom. H. Dunning, Jr.....	46
A-4 Ab Initio Calculation of the Reaction of Methyl Radical and Oxygen Molecule K. Kamiya, T. Asaba and H. Matsui .....	47
A-5 Infrared Laser Induced Reactions in Binary Polyatomic Systems J. Tardieu de Maleissye .....	48
A-6 Low Energy Crossed Beam Studies of the Reactions of Carbon Cations with Methane, Ethylene and Acetylene R. A. Curtis, D. M. Sonnenfroh and J. M. Farrar .....	49
A-7 Theoretical Studies of the Reaction of Atomic Oxygen ( <sup>3</sup> P) with Acetylene Lawrence B. Harding and Albert F. Wagner .....	50
A-8 Quasi-Classical Trajectory Study of Collision-Induced Dissociation in Collinear Atom-Diatomic Molecule Collisions Jack A. Kaye .....	51
A-9 Thermochemistry of the Decomposition of Energetic Materials: Application of the BAC-MP4 Method Carl F. Melius, J. Stephen Binkley, George F. Adams and Byron H. Lengsfeld III .....	52
A-10 Homogeneous Exchange Reaction Between Hydrogen and Deuterium Martin J. Rabinowitz and William C. Gardiner, Jr.....	53
A-11 Shapes of Activation Barriers for Hydrogen Atom Transfers from Curved Arrhenius Plots H. Furue and P. D. Pacey .....	54
A-12 Kinetics Controlled Completely by the Reaction Free Energy: Entropy Effects and Fast Endothermic Reactions Michael Meot-Ner (Mautner) .....	55

A-13	Quantum Mechanical Tunneling Reaction and Diffusion of H(D) Atoms in Solid Hydrogen at 4.2 and 1.9 K Tetsuo Miyazaki .....	56
A-14	Studies of Equilibria of the Reactions of Alkyl Radicals with Molecular Oxygen Irene R. Slagle and David Gutman .....	57
A-15	Kinetics and Energetics of Reactions of Hydrocarbon Free Radicals with O <sub>2</sub> in the Gas Phase R. Zellner, B. Fritz, K. Lorenz, M. Preidel and D. Rhäsa ...	58
A-16	Inverse Laplace Transformation of Rate Data for CH <sub>3</sub> + CH <sub>3</sub> + C <sub>2</sub> H <sub>6</sub> Joanne W. Austin, Nicholas J. B. Green and Michael J. Pilling .....	59
A-17	An Intramolecular Transition State Theory for Highly Vibrationally Excited Molecules: Application to a Model of OCS Michael J. Davis and Albert F. Wagner .....	61
A-18	Chemical Kinetic Mechanisms for Oxidation of Chlorinated Methanes D. L. Miller, M. Frenklach and R. A. Matula .....	62
A-19	Kinetic and Chemical Study of the Gas Phase Oxidation of Isobutane and Propane B. Vogin, G. Scacchi and F. Baronnet .....	63
A-20	Computer Program for the Calculation of Thermochemical Data of Molecules and Free Radicals in the Gas Phase, and Security Criteria of Chemicals Chantal Muller, Gerard Scacchi and Guy-Marie Come .....	64
A-21	Towards an Expert System for Gas Phase Reaction Mechanisms P. B. Ayscough, D. L. Baulch and S. Chinnick .....	65
A-22	A Reevaluation of Low Temperature Experimental Rate Data for the Reactions of O Atoms with Methane, Ethane and Neopentane N. Cohen .....	66
A-23	Sensitivity Analysis of Inhomogeneous Chemical Reaction Systems by the Method of Polynomial Approximation Fu-Tang Chen and Jenn-Tai Hwang .....	67
A-24	Dynamical Systems: Information from First Integrals Using Differential Topology F. G. Gascon and A. Gonzalez-Lopez .....	68
A-25	Gas-Phase Thermal Hydrogenolysis of Organic Chlorine Compounds Robert Louw, Peter Mulder, John H. M. Dijks and Jeffrey A. Manion .....	69

A-26	The Strainless C-(F) <sub>2</sub> (C) <sub>2</sub> (-CF <sub>2</sub> -) Group and the Strain Energies of Fluorinated Cycloalkanes Joel F. Liebman, William R. Dolbier, Jr. and Arthur Greenberg	70
A-27	The NBS Automated Chemical Kinetics Database System R. J. Cvetanovic .....	71

## POSTER SESSION B

	<u>Page</u>
B-1 A Comparison of Various Methods for Calculating Unimolecular Reaction Rate Constants Ralph E. Weston, Jr. ....	73
B-2 Decomposition of Alkoxy Radicals L. Batt .....	74
B-3 Unimolecular Decomposition of the Phenoxy Radical in Shock Waves Chin-Yu Lin and M. C. Lin .....	76
B-4 Pyrolyses of Toluene and Ethylbenzene K. M. Pamidimukkala and R. D. Kern .....	77
B-5 Pyrolysis of Acetylene in a Single-Pulse Shock Tube M. B. Colket, III .....	78
B-6 Heat of Formation of Radicals From Shock Wave Pyrolysis of Hydrocarbons R. Foon and R. J. Denning .....	79
B-7 Single Pulse Shock Tube Study on the Stability of Perfluorobromomethane W. Tsang .....	80
B-8 The Unimolecular Dissociation of Tetramethyldioxetane in the Gas Phase S. Ruhman, O. Anner and Y. Haas .....	81
B-9 An EPR Study of the Early Stages of TNT Thermal Decomposition J. T. Swanson, W. R. Carper, R. D. Murphy, J. A. Zirrolli, R. C. Dorey and S. R. Bosco .....	83
B-10 Gas Phase Unimolecular Dissociation Kinetics of Cyclic Perfluoro-Olefins Pradyot K. Chowdhury, K. V. S. Rama Rao and J. P. Mittal ...	84
B-11 Laser Powered Homogeneous Pyrolysis of Silane J. M. Jasinski and R. D. Estes .....	85
B-12 Laser Powered Homogeneous Pyrolysis of 1,3-Butadiene and 1,3-Vinylacetylene R. L. Woodin and K. A. Kajkowski .....	87
B-13 Primary Process in the Photolysis of Acetaldehyde G. N. Bagnall and H. W. Sidebottom .....	88

B-14	Correlation of Alkyl and Polar $\alpha$ -Substituents in the Gas Phase Pyrolysis Kinetics of Tertiary Alkyl Chlorides Gabriel Chuchani, Alexandra Rotinov, Ignacio Martin, Irama Avila and Rosa M. Dominguez .....	89
B-15	The Ion-Pair Mechanism Through Neighboring Group Participation in the Gas Phase Elimination Kinetics of (Dimethylamino) Alkyl Acetates Gabriel Chuchani, Alexandra Rotinov, Rosa M. Dominguez and Ignacio Martin .....	90
B-16	Yields of Molecular Hydrogen in the Elementary Reactions $\text{HO}_2 + \text{HO}_2$ and $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ Robert J. Glinski and John W. Birks .....	91
B-17	The Pressure Dependence of the Rate Constants for the Reactions $\text{HO}_2 + \text{HO}_2$ and $\text{HO}_2 + \text{NO}_2 + \text{M}$ at 298K .....	92
	Michael J. Kurylo and Philip Ouellette	
B-18	The IR Spectra, Geometry and Kinetics of the Dimer of $\text{HO}_2$ Radical Tai-Ly Tso and Edward K. C. Lee .....	94
B-19	Reactions of $\text{HO}_2$ with Free Radicals Michael Mozurkewich .....	95
B-20	Radiative Association: $\text{A}^- + \text{B} \rightarrow \text{AB}^- + \text{h}\nu$ , at 0.1 to 1 torr A. A. Viggiano, John F. Paulson, M. Henschman, Lucia Babcock and Charles Herd .....	96
B-21	A Closer Look at Radical Addition Reactions Anthony M. Dean .....	97
B-22	Direct Observation of Equilibration in $\text{H} + \text{C}_2\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_5$ Phillip D. Lightfoot, Mark Brouard and Michael J. Pilling ..	98
B-23	Hydrogen Atom Product in the Reaction of Ground State Atomic Oxygen with Ethylene John F. Smalley, Fred L. Nesbitt and R. Bruce Klemm .....	99
B-24	Picosecond Laser Studies of Collisionless UV Photodissociation of Gaseous Nitro-Compounds Jean-Claude Mialocq and John C. Stephenson .....	101
B-25	The Thermal Decomposition of $\text{S}_2\text{F}_{10}$ John T. Herron .....	103



# POSTER SESSION C

	<u>Page</u>
C-1 Temperature Dependence of Collisional Energy Transfer W. Forst .....	105
C-2 Theory of Collisional Energy Transfer Data Obtained From High-Overtone Spectroscopy Kieran Lim and Robert G. Gilbert .....	106
C-3 Vibrational Excitation of Small Polyatomic Molecules by Energy Transfer From Hot Hydrogen Atoms Ralph E. Weston, Jr. and George W. Flynn .....	107
C-4 Energy Transfer in Non-Reactive $H_2 + OH$ Collisions N. J. Brown and O. Rashed .....	108
C-5 Product State Distributions in the Vibrational Predissociation of the NO-Ethylene and NO-Ar Van Der Waals Molecules D. S. King and J. C. Stephenson .....	109
C-6 Internal Energy in Ion-Molecule Reactions: $NH_3^+ + D_2$ Paul R. Kemper and Michael T. Bowers .....	110
C-7 A Study of the Formation of $Cyclo-C_3H_3^+$ and $Cyclo-C_7H_7^+$ in the Gas Phase using a Triple Quadrupole Mass Spectrometer J. M. Tedder .....	111
C-8 Radiative Lifetimes and Reaction Rates of Metastable Electronic States in Small Molecular Ions Anthony O'Keefe and J. R. McDonald .....	112
C-9 Comparison Between the Mechanisms for the Formation of Electronically Excited Lead Oxide During the Reaction Between Lead Vapor and Either $^3\Sigma^- O_2$ or $^1\Delta O_2$ E. A. Dorko, J. P. Duray, C. M. Ritchey and J. W. Glessner .	113
C-10 Electronic Quenching of $IF(B^3\Pi(O^+))$ by $I_2$ M. R. Berman and P. D. Whitefield .....	115
C-11 Production of Electronically Excited States by Heterogeneous Catalysis Ang-Ling Chu, Robert R. Reeves and Judith A. Halstead .....	116
C-12 $BiF(AO^+, v')$ Radiative Lifetimes, Rates for $V \leftrightarrow T$ Transfer and Electronic Quenching H. Helvajian, J. S. Holloway, J. B. Koffend and R. F. Heidner III .....	117

C-13	Electronic-to-Vibrational Energy Transfer in the Deactivation O( <sup>1</sup> D) by CO <sub>2</sub> S. H. Bauer, J. Caballero, G. D. Greenblatt, M. Troller and J. R. Wiessenfeld .....	118
C-14	Resonance Optoacoustic Detection of NO by Double Modulation M. Seaver, T. J. Manuccia and J. R. McDonald .....	119
C-15	Vibrationally Excited Populations From i.r. Multiphoton Absorption: Optoacoustic and Reaction Yield Measurements John R. Barker, J-M. Zellweger and T. H. Brown .....	120
C-16	Vibrationally Excited Populations From i.r. Multiphoton Absorption: Infrared Fluorescence Measurements John R. Barker, J-M. Zellweger and T. H. Brown .....	121
C-17	First Observation of the Resolved Spectrum of the Formaldehyde (T1-S0) Transition from the Chemiluminescent Self-Reaction of Methoxy Radicals Dennis J. Bogan, Hung-tai Wang and William A. Sanders .....	122
C-18	Kinetic Studies of HO (A <sup>2</sup> Σ <sup>+</sup> ) Produced by KrF Laser Multi- photon Excitation of H <sub>2</sub> O P. Papagiannakopoulos and C. Fotakis .....	123
C-19	Time Resolved Optoacoustic Measurements of Vibrational Relaxation of Highly Excited Molecules Kenneth M. Beck and Robert J. Gordon .....	124

POSTER SESSION D

	<u>Page</u>
D-1 Kinetics of One-Electron Transfer Reactions Involving $\text{ClO}_2$ and $\text{NO}_2$ in Aqueous Solutions Robert E. Huie and P. Neta .....	126
D-2 Polymerization of $\text{NO}_2$ and $\text{NO}$ in a Supersonic Nozzle Expansion Mobuaki Washida, Hisanori Shinohara and Nobuyuki Mishi .....	127
D-3 Microwave Absorption Technique for Studying Secondary Electron Processes D. Nguyen, J. Sherwell and R. Cooper .....	128
D-4 Kinetics and Mechanism of Hexacyanoferrate (III) Oxidation of Arylthioacetic Acids C. Srinivasan and P. Subramaniam .....	129
D-5 Reactivity and Percentage Deamination in the Pulse Radiolysis of N-Alkyl Substituted Arylalkylamines Lalitha J. Mittal and Jai P. Mittal .....	130
D-6 Hydrogen Abstraction Rates by Resonance Stabilized Radicals in the Liquid Phase M. J. Manka, S. E. Stein and R. L. Brown .....	131
D-7 Benzene Hydrogenation Kinetics: A Transient Approach C. Mirodatos .....	132
D-8 Isotope Exchange Via Ionic Reactions Michael Henchman, John F. Paulson, David Smith and Nigel Adams .....	133
D-9 Slow Organic Electron Transfer Reactions: The Kinetic Consequences of Large Neutral-to-Ion Geometry Changes Michael Meot-Ner (Mautner) and Dan Rumack .....	134
D-10 Free Energy Surfaces with Multiple Wells. Slow Proton Transfer Reactions and Entropy Barriers Due to Steric Hindrance Michael Meot-Ner (Mautner) .....	135
D-11 The Proton in Multisolvant Clusters: The Acetonitrile-Water System Carol A. Deakyne and Michael Meot-Ner (Mautner) .....	136
D-12 How Does Solvation Affect Reactivity? P. M. Hierl, M. J. Henchman, A. A. Viggiano, A. F. Ahrens and John F. Paulson .....	137
D-13 Thermochemistry of Solvation of $\text{NO}_2^-$ and $\text{C}_6\text{H}_5\text{NO}_2^-$ by Polar Molecules in the Vapor Phase. Comparison with $\text{Cl}^-$ and Variation with Ligand Structure L. Wayne Sieck .....	138

D-14	Reaction Kinetics for Aerosol Formation in $O_3$ - $C_2H_4$ and $O_3$ - $C_2H_4$ - $SO_2$ E. R. Manzanares, Masako Suto and L. C. Lee .....	139
D-15	Three-Body Association Rate Coefficients as a Function of Temperature and Cluster Size A. A. Viggiano and John F. Paulson .....	140
D-16	On the Mechanism of the Reaction of Alkyl Ions with Alkylamines: Competing Proton Transfer and Condensation Reactions P. Ausloos and S. G. Lias .....	141
D-17	Picosecond and Nanosecond Laser Photolysis of Dinotrotoluenes in Solution B. B. Craig, S. Chattopadhyay and S. J. Atherton .....	142
D-18	Etching of $SiO_2$ by $CF_3$ Radicals N. Selamoglu, M. J. Rossi and D. M. Golden .....	143
D-19	The Reaction of $N_2O_5$ with Water on Carbonaceous Surfaces L. Brower, M. J. Rossi and D. M. Golden .....	144

POSTER SESSION E

	<u>Page</u>
E-1 The Shock Tube - Flash Photolysis - Resonance Absorption Technique for Measuring Bimolecular Rate Constants at High Temperatures J. V. Michael, J. W. Sutherland and R. B. Klemm .....	146
E-2 Laser Pyrolysis/Laser Fluorescence Measurements of High Temperature OH Reaction Rates with Propene, Butenes and Ammonia Gregory P. Smith, Jay B. Jeffries and David R. Crosley .....	147
E-3 Mechanism and Rate of Hydrogen Atom Attack on Toluene at High Temperatures D. Robaugh and W. Tsang .....	148
E-4 Reaction of Propane and Isopropyl Radicals with Atomic Oxygen Nobuaki Washida .....	149
E-5 The Reaction of Cyclopropyl Radicals with Oxygen Atoms P. Heinemann and K. Hoyer mann .....	150
E-6 Reactivity Trends in the Reactions of O( <sup>3</sup> P) with Alcohols and Ketones John M. Roscoe .....	152
E-7 The Arrhenius Parameters for the Reactions of Hydrogen and Oxygen Atoms with Five Fluoroethylenes Hironobu Umemoto, Ko-ichiro Sugiyama, Shigeru Tsunashima and Shin Sato .....	153
E-8 Production and Reaction of the Isopropoxy Radical R. Jeffrey Balla, H. H. Nelson and J. R. McDonald .....	154
E-9 Kinetics of the Isotope Exchange Reaction of <sup>18</sup> O with NO and O <sub>2</sub> at 298 K S. M. Anderson, F. S. Klein and F. Kaufman .....	155
E-10 A Kinetic Study of the Reaction OH + HNO <sub>3</sub> + M G. S. Jolly, G. Paraskevopoulos and D. L. Singleton .....	156
E-11 The Role of Selectivity for Radical Abstraction of Hydrogen Atoms in the Oxidation of Normal and Isopropylbenzene T. A. Litzinger, K. Brezinsky and I. Glassman .....	157
E-12 Reaction Kinetics of Br + HO <sub>2</sub> → HBr + O <sub>2</sub> D. W. Toohey, Wm. H. Brune and J. G. Anderson .....	158
E-13 Kinetics of Gas Phase Reactions of SIF <sub>2</sub> Andrew Freedman, Alan C. Stanton and Joda Wormhoudt .....	160

E-14	Kinetic and Mechanistic Studies of the OH + CO Reaction P. H. Wine, A. J. Hynes, R. J. Axtell and A. R. Ravishankara .....	161
E-15	The Temperature Dependence of Reactions of the SO Radical J. Brunning and L. J. Stief .....	162
E-16	Photoionization/Electron Cyclotron Resonance Detection of Gas Phase Radicals Robert A. Morris and David L. McFadden .....	163
E-17	Laser Induced Fluorescence Study of Pulsed Laser Photolysis of Acetaldehyde and Kinetics of HCO Bradley M. Stone and Edward K. C. Lee .....	164
E-18	The Photochemistry and Kinetics of Butadiyne in the Atmosphere of Titan S. Glicker and H. Okabe .....	165
E-19	Kinetics of Methylperoxy Radical Destruction by NO, Using DFMS G. L. Pellett and B. R. Adams .....	166
E-20	A Direct Kinetic Study of the Reaction $\text{Cs} + \text{I} + \text{He} \rightarrow \text{CsI} + \text{He}$ D. Husain, J. M. C. Plane and Chen Cong Xiang .....	167
E-21	Rate Coefficients for the $\text{CH}_3\text{SH}-\text{NO}_2$ Reaction R. Jeffrey Balla and Julian Heicklen .....	168
E-22	Laser Measurements of the Rate Constants for Reaction of CN Radical with Hydrocarbons William M. Jackson, Xuechu Li and Nahid Sayah .....	169
E-23	The Reactions of $\text{O}_2$ and $\text{HO}_2$ with $\text{CH}_2\text{OH}$ Radicals H. H. Grotheer, G. Riekert, U. Meier and Th. Just .....	172
E-24	Gas phase Oxidation Chemistry of Sodium J. A. Silver and C. E. Kolb .....	173
E-25	A New Look at High Temperature $\text{C}_2\text{H}_2/\text{O}/\text{-System}$ Incorporating Recently Obtained Information on Methylene Kinetics K. A. Bhaskaran, P. Frank and Th. Just .....	174
E-26	Measurement of Vibrational Groundstate Populations of HF Formed in F-Atom Reactions H. Heydtmann and J. Fendel .....	177
E-27	Rate Constants for Reactions of Phenyl Radicals with Acetylene, Ethylene and Benzene Askar Fahr, W. Gary Mallard and Stephen E. Stein .....	178

E-28	Measurement of the Fractional Yield of Methoxy from the Reaction F Plus Methane by Laser Induced Fluorescence and Chemiluminescence D. J. Bogan, B. E. Brauer, C. W. Hand, M. J. Kaufman, W. A. Sanders and H-t. Wang .....	180
E-29	Multiphoton Ionization Spectra of Radical Products in the F ( <sup>2</sup> P) + Ketene System: CH <sub>2</sub> F, CH and CF Jeffrey W. Hudgens, C. S. Dulcey and D. J. Bogan .....	181

**ABSTRACTS OF INVITED TALKS**



KINETIC AND PRODUCT STUDIES OF THE THERMAL DECOMPOSITION  
OF DIMETHYLSILANE IN A SINGLE PULSE SHOCK TUBE  
AND IN A STIRRED FLOW REACTOR

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Kinetic and product studies of the pyrolyses of dimethylsilane in a single pulse shock tube (1135-1290°K) and in a stirred flow reactor (890-1000°K) are reported. The shock induced reaction is accelerated by free radical and silylene chains which cannot be quenched by trapping agents. The mechanisms of the pyrolyses in various temperature ranges are discussed and modeling results for the stirred flow and shock tube reactions are shown to be in reasonable agreement with experimental observations. A mechanism for the decomposition of  $\text{Me}_2\text{Si:}$  to ethylene and acetylene via silarane is proposed, and the decomposition of ethylsilylene to  $\text{C}_2\text{H}_2$  and  $\text{SiH}_2$  is argued to be a 4-center concerted process. Arrhenium parameters for molecular elimination of methane from dimethylsilane are deduced ( $\log k_{\text{CH}_4} = 14.8 - 73,000/2.3RT$ ), establishing an activation energy for  $\text{CH}_3\text{SiH}$  insertion into the (C-H) bond of methane of  $E^\ddagger = 24.5$  kcal (pressure standard state).

## THERMOCHEMICAL KINETICS - A SUCCESS STORY ?

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This paper presents an analysis of the nature of the subject of Thermochemical Kinetics, the term coined by Sidney Benson some seventeen years ago. The subject is placed in the context of its relationship with various aspects of chemistry and its unifying themes are discussed.

To assist this exercise a number of examples are presented from our own and others' recent work. These examples cover a discussion of the stability of silenes (sila-olefins), silylenes and silicon containing cations.

KINETICS AND MECHANISM OF THE THERMAL DECOMPOSITIONS OF UNSATURATED  
ALDEHYDES: BENZALDEHYDE, CROTONALDEHYDE AND 2-FURALDEHYDE

M. A. Grela and A. J. Colussi

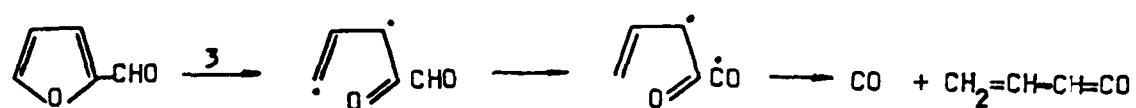
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The pyrolysis of benzaldehyde (BA), crotonaldehyde (CA) and 2-furaldehyde (FA) have been investigated in a flow reactor at very low pressures with modulated beam mass spectrometric analysis above 1040 K.

BA decomposes via C-H bond fission:  $\text{BA} \xrightarrow{1} \text{PhCO} + \text{H}$ , between 1170-1250 K followed by rapid decarbonylation of benzoyl radicals. Species at  $m/z = 28$  and 77 were the exclusive products with  $\log(k_1, \text{s}^{-1}) = 15.3 - 82.6/\theta$  ( $\theta = 4.575 \times 10^{-3}T$  Kcal/mol), which leads to  $\Delta H_f(\text{PhCO}) = 25.0 \pm 2.0$  Kcal/mol, confirming the above analysis.

Crotonaldehyde,  $\text{CH}_3\text{-CH}=\text{CH}-\text{CHO}$ , decomposes at lower temperatures (1040-1180 K) yielding CO and a species of mass 42 as the sole products. Pyrolysis of labelled crotonaldehyde,  $\text{CH}_3\text{-CH}=\text{CH-CDO}$ , led to fragments at 28 and 43. No evidence of free radicals of mass 41 was found in either case. Accordingly we propose a concerted three-center H-atom transfer for reaction 2:  $\text{CA} \xrightarrow{2} \text{CH}_3\text{-CH}=\text{CH}_2 + \text{CO}$  with  $\log(k_2, \text{s}^{-1}) = 13.5 - 60.5/\theta$ .

Finally, FA decomposes between 1090-1190 K giving rise to fragments at  $m/z = 28, 40$  and 68. The temperature dependence of the signal of mass 68 suggests an intermediate species isomeric of but more stable than furan<sup>1</sup>. Time of flight analysis of the products also reveals that the peak of mass 40 is a fragment of the 68 ion rather than a different product. On this basis we propose the following mechanism for the decomposition of FA:



We assign the product of mass 68 to vinylketen and identify the overall rate to be the ring opening step with  $\log (k_3, \text{s}^{-1}) = 15.3 - 67.0/0$ .

- 1) M. A. Grela, V. T. Amorebieta and A. J. Colussi, *J. Phys. Chem.* 89  
(1985)

# HYDROGEN TRANSFER BETWEEN POLYAROMATIC MOLECULES

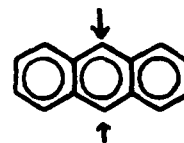
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We are currently engaged in a program intended to clarify the chemistry occurring in organic fluids at elevated temperatures (300°-600°C). Hydrogen transfer readily occurs in these environments and can serve as the critical step in a wide range of structural transformations. Mechanisms of H-transfer are a matter of considerable current speculation.

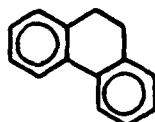
To clarify these mechanisms we have determined the kinetics of

H-transfer to the meso (9,10) positions of anthracene (

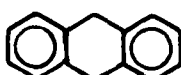


)

from 9,10-dihydrophenanthrene (



) and 9,10-dihydroanthracene

(  ). Mechanisms of these reactions were sufficiently

uncomplicated to allow a thorough mechanistic analysis.

This analysis revealed the significance of H-atom transfer from one closed shell molecule to another ("molecular disproportionation") as the predominant radical initiation step and showed the  $\beta$ -H-transfer by a radical to a molecule ( $\beta$ -H transfer) is a key chain transfer step. Rate constants for these reactions have been derived from these studies which will be useful in developing estimation methods for rates of related reactions.

Work supported by the Gas Research Institute.

KINETICS OF PRIMARY PROCESSES IN THE PYROLYSIS  
OF CYCLOPENTANES AND CYCLOHEXANES

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Studies of the thermal unimolecular decomposition of cyclopentane, methylcyclopentane, vinylcyclopentane, cyclohexane, methylcyclohexane, and vinylcyclohexane have been carried out at temperatures in the range 900-1223 K using the technique of very low-pressure pyrolysis (VLPP). The results show that ring-opening isomerization to open-chain alkenes is the major primary process for each of the above reactants. Under the experimental conditions the alkenes undergo further decomposition via C-C bond fission and/or retro-ene processes. Application of RRKM theory shows that the VLPP data (fall-off regime) are consistent with the following high-pressure rate expressions (at  $\langle T \rangle = 1100$  K) for overall decay:

$$\log (k/s^{-1}) = (16.8 \pm 0.3) - (355 \pm 8)/\theta \text{ for cyclopentane}$$

$$\log (k/s^{-1}) = (16.9 \pm 0.3) - (361 \pm 8)/\theta \text{ for cyclohexane}$$

$$\log (k/s^{-1}) = (16.4 \pm 0.3) - (343 \pm 8)/\theta \text{ for methylcyclopentane}$$

$$\log (k/s^{-1}) = (16.4 \pm 0.3) - (343 \pm 8)/\theta \text{ for methylcyclohexane}$$

$$\log (k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta \text{ for vinylcyclopentane}$$

$$\log (k/s^{-1}) = (16.0 \pm 0.3) - (309 \pm 8)/\theta \text{ for vinylcyclohexane}$$

where  $\theta = 2.303RT$  kJ/mol. The A factors were based on known values for C-C bond fission in alkanes and alkenes. Comparison of the activation energies for the unsubstituted and methyl-substituted cyclanes with those for the vinyl-substituted cyclanes reveals that the effect of the vinyl substituent is close to the established value for the allyl resonance energy. This evidence supports the assumption of a biradical mechanism for the ring opening of medium-sized cyclanes.

SOME KINETIC AND THERMOCHEMICAL ASPECTS OF  
SODIUM IN THE STRATOSPHERE

by

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and

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\*Acknowledgements: This work has been funded in part by Grants from the U.S. Army Research Office (Grant No. DAAG-29-82-K0043) and the National Scientific Foundation (Grant No. CHE-8403761).

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Metals present in the stratosphere arise mainly from meteoroid ablation above 90 km. They may also be injected by volcanism or artificially in rocket releases. Observations of Na at 90 km estimate concentrations of  $1-3 \times 10^4$  Na/cc. Recent calculations suggest that salts of Na and Na atoms may play an important role in the stratospheric chemistry related to ozone. We report here an extension of these calculations to show that starting at 30-35 km, the polymerization of NaX (X = OH or Cl) becomes a very fast process, producing  $(\text{NaX})_m$  where  $m > 1000$ . One effect of this polymerization is to reduce  $(\text{NaX})$ , and  $(\text{NaX})_2$  to steady state concentrations below 1 particle/cc where they cease to affect  $\text{O}_3$  chemistry.



## The $F + H_2$ Potential Energy Surface: The Ecstasy and the Agony

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A theoretical study has been conducted to clarify the discrepancy between ab initio predictions of the entrance channel barrier in the  $F + H_2$  reaction and the experimentally observed thresholds for product formation. New results using two different models are in better agreement with the experimental exoergicity and predict a zero-point energy corrected barrier of 2.0 kcal mole<sup>-1</sup>. Estimates of the resulting reaction cross section and thermal activation energy suggest that this value differs from experiment by about 0.5 kcal mole<sup>-1</sup>. The theoretically predicted isotope effect on the thermal activation energy is larger than either of the recently suggested experimental values, which, however, are subject to large uncertainties.

ELEMENTARY REACTIONS IN COMPRESSED GASES AND LIQUIDS:  
FROM COLLISIONAL ENERGY TRANSFER TO DIFFUSION CONTROL

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Elementary chemical processes such as unimolecular dissociation and isomerization, atom and radical recombination, and photo-dissociation have been studied experimentally over wide density ranges, from low pressure gases via highly compressed gases into compressed liquids. The density dependence reveals various aspects of reactant-solvent interactions: isolated molecule behaviour and collisional energy transfer control at low gas pressures, control by intramolecular processes in high pressure gases, the contribution of van der Waals complexes in high pressure gases, diffusion control and energy relaxation in the liquid phase, solvent shifts in van der Waals complexes and liquid cages. These observations are represented by simple models and elaborate theories. Particular emphasis is given to halogen dissociation, recombination, and photolysis, and to the photoisomerization of trans-stilbene and diphenylbutadiene.

Comparison of Thermodynamics and Kinetics for Some Important  
Bond-Making and-Breaking Processes in Organic Chemistry

by

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The relationship between reactivity, as expressed through kinetics, and stability as expressed through thermodynamics, is one of the most fundamental in chemistry. However, there are relatively few cases where an extensive collection of rate and equilibrium data are available for the same simple process of bond making and breaking. Thus, it is common practice in physical organic chemistry to compare the relatively accessible rates ( $\Delta G^\ddagger$ ) for the displacement reactions of nucleophiles on carbon centers with the basicities of those nucleophiles as represented by their  $pK_a$ 's (or free energies of ionization) in their interactions with protons in solution.

This lecture will present comparison of activation parameters ( $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ ) with corresponding thermodynamics of reaction for simple bond-forming and bond-breaking reactions. These include the Menschutkin quaternization reaction and more recent studies of the direct coordination reaction between resonance-stabilized carbocations and carbanions in solution. Correlation of these properties with each other in response to structural change will be presented and compared with more familiar correlations of rates vs.  $pK_a$ 's.

UNIMOLECULAR AND INTRAMOLECULAR DYNAMICS. RELATIONSHIP TO  
POTENTIAL ENERGY SURFACE PROPERTIES

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Modern experimental measurements provide detailed information concerning the relationship between unimolecular reaction attributes and potential energy surface properties. A challenge for theorists is the development of accurate theoretical models and numerical methods which can be used to interpret experimental results in terms of potential energy surfaces as well as predicting relationships between unimolecular dynamics and features of potential energy surfaces.

Classical trajectories have been widely used to model unimolecular and intramolecular processes, and a critique of this method will be given. Three applications of the classical trajectory method will be considered. Energies for the vibrational levels of the model  $\text{H-C-C} \rightarrow \text{H} + \text{C=C}$  Hamiltonian are calculated from quasiperiodic classical trajectories with the semiclassical quantization condition and compared with the exact quantum mechanical values. Above the unimolecular threshold a quasiperiodic trajectory gives the value for the real component of the eigenvalue. Classical and quantal studies of the decay of coherent states (wave packets) will also be compared. The zero-point energy problem involved in using classical trajectories to compute unimolecular rate constants as a function of energy and angular momentum will be discussed.

A fascinating question in unimolecular rate theory is whether compound state (Feshbach) resonances are involved in the dissociation of molecules with covalent type intramolecular potentials. A number of classical and quantal theoretical studies suggest these states exist. Experimental studies

such as chemical activation and collision-free overtone excitation seem to be nearly insensitive to their presence. The relationship between intramolecular relaxation for bound molecules and unimolecular decomposition dynamics (e.g., compound state resonances) will be discussed. Particular intramolecular properties which have been studied are stretch-bend coupling in hydrocarbons and the heavy-atom effect.

The accuracy of classical trajectories for calculating energy and angular momentum partitioning in unimolecular reactions will be discussed. To analyze exit-channel effects and angular momentum constraints a combined statistical/trajectory approach is very useful.

## THE DISSOCIATION DYNAMICS OF ENERGY SELECTED IONS

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The study of energy selected (or state selected) ions has been a thriving research area since the advent of photoelectron photoion coincidence (PEPICO) spectroscopy. When a molecule is photoionized with a monochromatic beam of vacuum UV photons of energy  $h\nu$ , ions in a range of internal energies from 0 to  $h\nu - IP$  are produced. In order to state select these ions, we measure them in coincidence with energy analyzed electrons. These energy selected electrons determine not only the ion energy, they also provide us with a precise start time for measuring the ion time-of-flight (TOF). State selection is assured because only those ions associated with the detected electrons are recorded in the coincidence circuit.

All of the dynamical information is contained in the ion TOF distribution. The fragment ion originating from a slowly dissociating parent ion (i.e. from a parent ion which moves some distance in the acceleration region before fragmenting) will have an asymmetric TOF distribution. Dissociation rates as a function of the ion internal energy,  $k(E)$ , can be measured over a range of rates from  $10^4$  to about  $3 \times 10^6 \text{ sec}^{-1}$ . Comparison of these rates with those predicted by the statistical theory of unimolecular reactions (the RRKM theory or the quasi-equilibrium theory) allows us to determine structures of transition states, the energy and structure of products, as well as the mechanism for the reaction. Ionic reactions of such ions as phenol, nitrobenzene, methyl nitrite ( $\text{CH}_3\text{ONO}^+$ ) are often very complicated and the measured rates tell us a great deal about what happens in the dissociation process. Often these ions isomerize to more stable structures prior to dissociation. In addition, the stable ionic structures are often very different from the most stable neutral structures.

EMPIRICAL APPROACH TO SUBSTITUENT RATE EFFECTS IN  
[3,3]-SIGMATROPIC SHIFTS UTILIZING THE THERMOCHEMISTRY OF COUPLED  
NONCONCERTED ALTERNATIVE PATHS. III.

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Substituents affect the structure of the [3,3]-sigmatropic shift transition state as deduced from alpha secondary deuterium kinetic isotope effects. Since this variation is interpretable in terms of the relative stability of bond breaking and bond making nonconcerted alternatives as suggested by Thornton, the rates of these reactions were correlated with the free energies of formation of the transition states for nonconcerted bond breaking and bond making relative to reactant and with the free energy of reaction. The correlation equations were derived from hyperbolic paraboloid models of the energy surface. These are discussed in terms of recent attempts to apply Marcus Theory to pericyclic thermal reactions. The facility of the synthetically useful Ireland-Claisen rearrangement and the biologically important conversion of chorismate to prephenate are discussed in terms of the current model.

## ENERGY TRANSFER

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In most work a clear distinction has been made between intra and intermolecular energy transfer but there has been some discussion of collision induced intramolecular energy transfer. While we will be mainly concerned with intermolecular transfer between molecules in their ground electronic states we note that for highly energised molecules of reasonable size (more than 6 or 7 atoms) intramolecular energy randomisation takes place on the pico second timescale. There is little reliable experimental evidence for various kinds of pathological behaviour though the experimental base for these findings is still small. Interestingly trajectory and other calculations (a more specialised experimental science) often indicate pathological behaviour especially for small molecules.

The field of intermolecular energy transfer is very active at present and also rather fluid. Nevertheless there are some general trends that have emerged. For ground state molecules vibrational vibrational energy transfer between highly energised molecules and polyatomic receiver molecules is responsible for the relatively large values of  $\Delta E$  and the magnitude of  $\Delta E$  increases with the complexity of the molecule to which the energy is transferred. There is less certainty about the temperature coefficient of  $\Delta E$  or even its sign. It is also interesting to observe that recent work appears to support somewhat smaller average values of  $\Delta E$  than previously.



Some examples of reported work will be discussed and we will present results from a conventional thermal study on the decomposition of chlorocyclobutane which yields values of  $\Delta E$  for a series of collider gases.

LARGE MOLECULE ENERGY TRANSFER:  
NEW TECHNIQUES AND NEW CONTROVERSIES

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Up until the last few years, most information concerning large molecule energy transfer was obtained in unimolecular reaction studies. Recently, new methods have been applied to the problem, leading to results that differ in some respects from the older studies. But the new results also differ from one another. Out of these differences have grown at least three important controversies, which can be stated as questions:

- (1) How large is  $\Delta E$ , the energy-loss step-size?
- (2) Does  $\Delta E$  depend on the vibrational energy of the excited molecule?
- (3) Does  $\Delta E$  increase, decrease, or stay the same when the bath temperature is increased?

The answers to these questions will have major effects on virtually all applications of unimolecular rate theory and they will prove to be important in laser induced chemistry, as well.

The first part of this paper will consist of a description of the controversies in terms of the experimental methods used and their respective weaknesses and strengths. The second part of the paper will present brief descriptions of several still newer techniques that promise to add to the controversies, if not resolve them. The last part of the paper will describe new (ie. preliminary) results obtained in our laboratory using infrared multiphoton absorption for preparation of the excited molecules and infrared fluorescence for monitoring their vibrational excitation and energy transfer properties.

## Vibrational Relaxation of Chemical Bonds in Liquids and on Surfaces

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Molecular Spectroscopy Division

The available information on the de-excitation rates ( $k_v$ ) of vibrational modes for ( $T$  = room temperature) liquids, solids, and surface bonds at the solid-vacuum and solid-liquid interface is reviewed. Compared to gas phase rates, the condensed phase data are sparse and unreliable. Reported energy relaxation rates based on time-resolved measurements range from  $k_v = 2 \times 10^8 \text{ s}^{-1}$  to  $k_v > 10^{12} \text{ s}^{-1}$ . Certain indirect methods of estimating vibrational energy transfer (VET) rates, such as interpreting spectral linewidths as caused by vibrational energy relaxation, are questionable.

VET in liquids has been interpreted in terms of gas phase models: a liquid phase "binary collision rate" is calculated (typically  $k_{\text{coll}} = 2 \times 10^{12} \text{ s}^{-1}$ ), and a deactivation probability ( $P = k_v/k_{\text{coll}}$ ) defined. Remarkably, usually  $P_{\text{liquid}} \approx P_{\text{gas}}$ . By contrast, VET in solids is usually discussed in terms of multiphonon relaxation, which is analogous to intramolecular vibrational relaxation (IVR) in highly excited gas phase polyatomic molecules. Vibrational damping of bonds on solid surfaces has been interpreted in terms of electron-hole pair formation (on metals), image-dipole formation, and coupling to substrate modes via an IVR-type treatment. Recent measurements of VET rates for certain high frequency vibrations, e.g.,  $\text{OH}(v=1)$ , in gases, liquids, solids, and at surfaces show that the relaxation rates in these different phases are comparable, suggesting the need for a unified approach to interpreting VET.

In gases, bimolecular chemical reaction rates can be greatly influenced by reactant vibrational excitation in particular bonds; also, non-thermal vibrational excitation of reaction products is common and useful (e.g., chemical lasers). In condensed phases, the slow VET rates (e.g., slow compared to rates for molecular reorientation or diffusion over a distance of several molecular diameters) seen for some high frequency vibrations suggest that similar chemically interesting effects of non-thermal vibrational excitation could occur, for instance, in surface catalyzed reactions.

PREDICTION OF RATE CONSTANTS FOR IONIC REACTIONS  
IN THE GAS PHASE AND IN SOLUTION

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Ionic reactions present an especially interesting challenge in attempts to predict rate constants. In solution, problems related to solvation are difficult to analyze, whereas in the gas phase, the physical dynamics problems are less straightforward. Nevertheless, significant progress is being made in both areas. Aspects of nucleophilic displacement and proton transfer reactions are discussed.

MEASUREMENT OF ABSOLUTE PROPAGATION AND TERMINATION  
RATE CONSTANTS FOR ALKYLPEROXYLS IN SOLUTION BY THE  
HYDROPEROXIDE METHOD

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Kinetic and product studies of liquid phase autoxidations in the presence of high concentrations of alkyl hydroperoxides have enabled absolute propagation and termination rate constants for alkylperoxyls to be measured. A large number of rate constants and activation parameters have been accumulated over the past few years by this technique and the highlights of this work are presented here.

KINETICS AND MECHANISMS OF INORGANIC REACTIONS IN  
AQUEOUS SOLUTIONS: INTERMEDIATES

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This status report concerns transient intermediates in inorganic reactions, with particular but not exclusive considerations of radical species. The involvement of such intermediates can be documented by conventional studies of thermal reactions combined with the use of newer pulse methods for the direct generation and detection and study of the reactive transients. Examples chosen from transition metal chemistry, with especial emphasis on Cr, Co, Rh, and Ni complexes will be cited.

Measurement and Understanding of Gas-Phase  
Bimolecular Reactions

F. Kaufman, Department of Chemistry

Progress and prospects in the experimental measurement of fast, elementary rate processes will be summarized. Our qualitative and quantitative understanding of these processes will be examined in some detail using the following examples: (1) The OH + H<sub>2</sub> reaction<sup>1</sup> where ab initio quantum theory plus variational transition state theory has been applied; (2) The reaction of OH with substituted methanes and ethanes<sup>2</sup> where semi-empirical thermochemical kinetics has been used to predict the A-values of Arrhenius expressions; (3) The high pressure,  $k^\infty$ , values of simple recombinations such as O + NO and O + O<sub>2</sub>, as studied by isotope exchange;<sup>3</sup> and (4) the reaction/energy transfer process of N<sub>2</sub>(A<sup>3</sup>Σ<sub>u</sub><sup>+</sup>) with O<sub>2</sub>(X) and with O(<sup>3</sup>P) where product channels have been determined.<sup>4</sup> The general conclusion is that while close interaction of experimentalists and theorists is highly desirable, the results have, so far, been disappointing.

<sup>1</sup>A. R. Ravishankara, J. M. Nicovich, R. L. Thompson, F. P. Tully, J. Phys. Chem. 85, 2498 (1981); A. D. Isaacson, D. G. Truhlar, J. Chem. Phys. 76, 1380 (1982).

<sup>2</sup>K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, F. Kaufman, J. Phys. Chem. 88, 1222 (1984).

<sup>3</sup>S. M. Anderson, F. S. Klein, F. Kaufman, J. Chem. Phys. submitted, Also see contributed paper

<sup>4</sup>J. M. Thomas, F. Kaufman, J. Chem. Phys., submitted.

# **THEORETICAL CHARACTERIZATION AND CALCULATION OF POTENTIAL ENERGY SURFACES FOR CHEMICAL REACTIONS\***

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The past few years has witnessed the development of a number of important techniques for the characterization and calculation of potential energy surfaces for chemical reactions, e.g.,

(1) Methods are now available for the location of saddle points and the determination of reaction paths for chemical reactions. These techniques provide a means of systematically characterizing the most critical features of molecular potential energy surfaces.

(2) Great strides have been taken in improving the efficiency of the computational techniques and algorithms used to compute the energetics of chemical reactions. These techniques will greatly extend the number of systems for which accurate molecular potential energy surfaces are known.

Exploitation of these techniques can be expected to greatly increase our understanding of the energetics and mechanisms of chemical reactions.

A number of examples will be chosen to illustrate the application of the techniques noted above to reactions involving three and four atoms. The emphasis here will be on the general concepts developed from, rather than on the numerical details of, the calculations. Topics to be discussed include trends in homologous series, description of electron-jump mechanisms, reactions involving multiple reaction pathways, pseudo-three body reactions, reactions with non-least motion pathways and radical-radical processes. In so far as possible, examples will be chosen to represent general classes of reactions. While the reactions chosen cannot be considered representative of all of chemistry, as we shall see, they provide a wide diversity of reaction types.

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\*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under Contract W-31-109-Eng-38.



# LASER STIMULATION AND OBSERVATION OF BIMOLECULAR REACTIONS

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Traditionally, the energy dependence of the reaction rate of bimolecular reactions is studied under conditions in which the rate of reaction is slow compared to that of collisional energy transfer. Under these conditions, the energy of the reactants is characterized by a temperature. The Arrhenius parameters obtained in this way, however, contain no direct information on how the various degrees of freedom of the reacting molecules and in the "activated complex" contribute to the overcoming of the potential barriers of product formation in the chemical reaction. Investigations on the chemical reactivity under a wide range of conditions such as specific excitation of the reactants give therefore important insights into the microscopic dynamics of bimolecular reactions.

The paper describes experimental results on the effect of selective translational, rotational, vibrational and electronic excitation of reactants in bimolecular reactions using flow systems, crossed molecular beams, UV- and IR laser excitation and reactant and product detection by time-resolved atomic line resonance absorption, mass, LIF and CARS spectroscopy. The experimental results are compared with the results of quantum and quasi-classical trajectory studies on ab initio potential surfaces and thermal rate parameters.

POSTER SESSION A

General Classical Variational Theory of the Rates of Atom-Diatom Reactions. G. W. Koeppl<sup>a</sup> and D. I. Sverdlik, Queens College of the City University of New York, Flushing, NY 11367.

The classical variational theory of chemical reaction rates gives the rate as the equilibrium flux of systems through a trial surface in the phase space of the reaction system. The surface divides the phase space into reactant and product regions and is varied to obtain a minimum upper bound for the rate of product formation. For bimolecular reactions of the type  $A+BC \rightarrow AB+C$ , we have derived expressions for the microcanonical and canonical formulations of this theory which give the energy dependent mean reaction cross section ( $\langle S^{\ddagger}[E] \rangle$ ) and canonical rate constant ( $k^{\ddagger}[T]$ ), respectively, for the most general surface defined by configuration space coordinates. We have obtained the differential equations which define the best dividing surfaces of this type for both microcanonical and canonical cases. We have developed a numerical method based on a simplex algorithm which permits an efficient determination of the coefficients in the second order expansion of the dividing surface. The method is being applied to the  $H+H_2$ ,  $H+I_2$ , and  $H+HBr$  abstraction and exchange reactions. We are determining the energies and temperatures up to which the mean reaction cross section and canonical rate constant converge to classical mechanical trajectory results.

# Theoretical Study of the $H + XY$ Reactions ( $X, Y = F-I$ )\*

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Theoretical Chemistry Group

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## Infrared chemiluminescence studies of the abstraction reactions



and



( $X, Y = F-I$ , with  $X$  less electronegative than  $Y$ ) have a bimodal energy distribution in the  $HY$  product. This suggests that microscopic branching is occurring in the production of  $HY$ , with the two reaction pathways corresponding to: 1) direct attack by the hydrogen atom at the  $Y$ -halogen atom, and 2) initial attack by the hydrogen atom on the  $X$ -halogen atom, followed by migration of the hydrogen atom to the  $Y$ -halogen atom. Trajectory studies on LEPS potential energy surfaces had led to the proposal that the microscopic branching in the  $HY$  product was largely a dynamical effect. Further, crossed molecular beam studies of these reactions have been interpreted to imply that the lowest energy reactive complex has the least electronegative halogen atom in the central position and that the transition state geometry becomes increasingly non-collinear as the central halogen atom varies from chlorine to iodine.

In order to provide a more complete description of the energetics and mechanisms of the above reactions, large-scale configuration interaction calculations have been carried out on the  $HXY$  systems to characterize the bound species and saddle points on the potential energy surfaces. The results from the calculations show these reactions to have "early" transition states. Further, as the atomic number of the central halogen increases, the transition state geometries become more bent and the barrier heights decrease. These results are in general accord with the experimental observations noted above. These calculations indicate that the indirect  $HY$  microscopic branch in these reactions arises from the shape of the potential energy surfaces, not from just a dynamical effect. The reaction path for a representative system will be presented.

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\*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under Contract W-31-109-Eng-38.

## Theoretical Study of the Li + HF Reaction\*

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The reaction of lithium atoms with hydrogen fluoride,



is representative of a class of reactions which are thought to proceed by an "electron-jump" type mechanism. A theoretical study of this reaction was reported by Chen and Schaefer in 1980; simultaneously, a molecular beam study of the Li + HF reaction was reported by Lee and coworkers.

We have computed a complete reaction path for this reaction - the intrinsic reaction path of Fukui (1970). We calculated both the energy and fundamental frequencies along the reaction path. Contrary to the conclusions drawn by Chen & Schaefer, we found that the reaction path involves a "front-side" displacement of the H atom by the Li atom. The electron transfer, which occurs just before the saddle point, is found to be predominately from the Li atom to the (positively charged) H atom. This is expected to be the mechanism for many electron-jump reactions; it minimizes distance over which the charge transfer must take place while avoiding the high energy "backside" approach.

Time and space permitting, calculations on other reactions in the the M + HX (M = metal, X = halogen) series will also be presented.

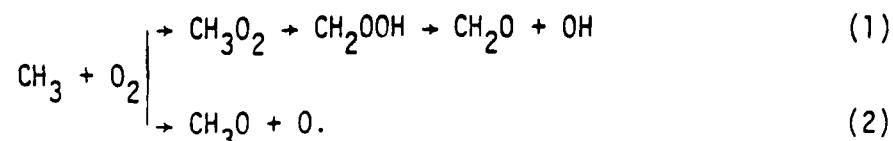
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\*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under Contract W-31-109-Eng-38.

# Ab Initio Calculation of the Reaction of Methyl Radical and Oxygen Molecule.

K.Kamiya, T.Asaba and H.Matsui  
(Dep. of Reaction Chemistry, Univ. of Tokyo)

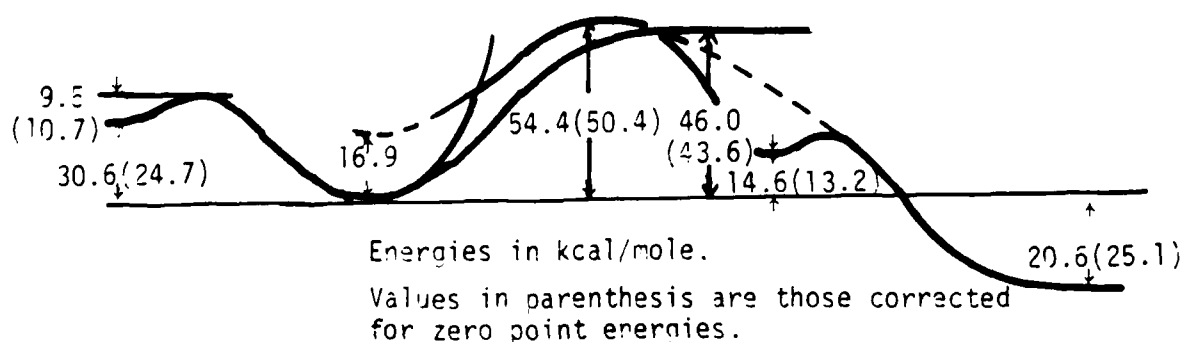
Two paths were proposed for the reaction of methyl radical and oxygen molecule, i.e.



This reaction system has been treated by means of ab initio calculations to evaluate the energies of the intermediates and the transition states. The program used for calculations was GAUSSIAN 80.

For the optimization of molecular structures the energy gradients were minimized by use of "Unrestricted Hartree-Fock" method with mainly 3-21G\* as the basis function. On the molecular structures thus determined the energies were calculated by use of 6-31G\*\* and the correlation energies were evaluated up to the third order by Moller-Plessett perturbation method. The normal mode analysis was performed by the numerical integrations of the energy gradients by use of 3-21G\* for the transition state of isomerization reaction of  $\text{CH}_3\text{O}_2$  into  $\text{CH}_2\text{OOH}$  and 3-21G for other molecules, respectively.

Results are shown in the figure. In the path of the transition,  $\text{CH}_3\text{O}_2$  to  $\text{CH}_2\text{OOH}$ , the potential surfaces of the excited electronic state,  $^2\text{A}'$ , and the ground state,  $^2\text{A}''$ , are crossing. The adiabatic excited energy is calculated as 16.9 kcal/mole by use of MP3/6-31G\*. As can be seen in the figure, the energies of the transition states are considered to be very close, since the uncertainty of calculations is evaluated to ca. 10 kcal/mole.



# INFRARED LASER INDUCED REACTIONS IN BINARY POLYATOMIC SYSTEMS

J. TARDIEU de MALEISSYE - Université P. et M. Curie - PARIS

Among laser induced chemical processes, photosensitized infrared laser induced reactions represent particular systems in which the energy absorption steps are clearly separated from the reactive steps.

In the case of binary gaseous systems under heat bath conditions exposed to high photon flux, the Boltzmann distribution of energy of the molecules may be disturbed mainly in the high energy tails, if the ratio of vibration-vibration to vibration-translation relaxation rates is high enough. As a result, this perturbation of the energy distribution may manifest itself in the overall kinetic behavior.

The decomposition kinetics of some hydrocarbons photosensitized by  $\text{SF}_6$  as well as the bireactive  $\text{SO}_2\text{-CO}$  system, where  $\text{SO}_2$  both plays the role of absorber and reactant, have been investigated under CW irradiation of a  $\text{CO}_2$  laser under heat bath conditions. The partial pressure of absorber was constant ( $p_{\text{SF}_6} = 3.3$  torrs,  $p_{\text{SF}_6} = 300$  torrs) and the overall rates of decomposition of  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{iC}_4\text{H}_{10}$ ,  $\text{nC}_4\text{H}_{10}$  as a function of their partial pressures were observed.

The rate of formation of  $\text{CO}_2$  from  $\text{SO}_2\text{-CO}$  irradiation was also investigated. During these experiments, the output laser power was changed from 380 to 100 Watts.

All the binary systems that we have studied exhibit a maximum rate of decomposition (hydrocarbons) or formation ( $\text{CO}_2$ ) for a given initial pressure of hydrocarbon or  $\text{CO}$ . After the maximum, the reaction rate decreases, very rapidly in some cases. For instance, the increase of 40% in the partial pressure of  $\text{iC}_4\text{H}_{10}$  after its maximum, results in a complete inhibition of its decomposition.

Furthermore, the maximum rate of decomposition in the case of  $\text{C}_2\text{H}_6$  is linearly dependent on the square of the incident laser power. It is possible to interpret both of these features by considering a distribution of the energy captured within the heat bath,  $\sum nq$ , between the two collisional partners A, B, where A plays the role of absorber:

$$\sum nq = (n_A q)_A + (n_B q)_B$$

Under these conditions, the overall reaction rate is proportional to the product of the internal energies present in each polyatomic species, leading to a parabolic form:

$$R_g = k(n_A q)_A (n_B q)_B = k_1 (n_B q)_B - k(n_B q)_B^2$$

At the maximum reaction rate, the distribution of energies between the two partners is given by  $(n_B q)_B$  and  $(n_A q)_A = (n_B q)_B$ ,

$$\text{then } [R_g]_{\max} = k [P / (1 + P)] (\sum nq)^2$$

These conclusions can be also represented in simplified kinetic form.

LOW ENERGY CROSSED BEAM STUDIES OF THE REACTIONS OF CARBON  
CATIONS WITH METHANE, ETHYLENE, AND ACETYLENE, R.A.  
Curtis, D.M. Sonnenfroh, and J.M. Farrar, Department  
of Chemistry, University of Rochester, Rochester, NY 14627

We have employed an ion beam technique to measure differential cross sections for the reactions of  $C^+$  with  $CH_4$ ,  $C_2H_4$ , and  $C_2H_2$  over the relative energy range from 0.5 to 2.4 eV. Hydride abstraction reactions are important only for  $CH_4$  and proceed as direct rebounding collisions. The dominant channels for these systems are condensation reactions occurring with the formation of new carbon-carbon bonds. The condensation reactions with  $CH_4$  to form  $C_2H_2^+$  and  $C_2H_3^+$  proceed through the formation of a long-lived  $C_2H_4^+$  intermediate at low collision energies. Center of mass angular distributions for these reactions exhibit distinctive features which correlate with the transition state geometries for hydrogen atom or molecular hydrogen elimination from the complex. The kinetic energy distributions for  $C_2H_3^+$  formation as a function of incident energy demonstrate a functional dependence on the fraction of the total available energy in translation.  $C_2H_2^+$  production, however, behaves anomalously at high energy, suggestive of an "osculating" prolate complex with a lifetime comparable to a rotational period, and decaying with synchronous ejection of two hydrogen atoms. The condensation reactions with ethylene and acetylene exhibit features similar to the methane system, but the differing geometries for unimolecular decay and the greater molecular complexity yield energy dependent asymmetries somewhat different from the methane system. The lifetime information extracted from these angular distributions as well as the form of the recoil energy distributions provides insight into the nature of statistical energy partitioning in the decomposing intermediate complex.



# Theoretical Studies of the Reaction of Atomic Oxygen ( $^3P$ ) with Acetylene\*

Lawrence B. Harding and Albert F. Wagner

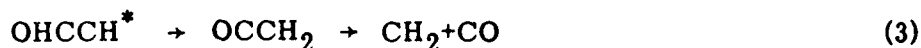
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Ab initio, configuration interaction (RHF+1+2) calculations using a polarized double zeta basis set will be reported on the transition states and intermediates of the reactions,



Addition, (1), is found to proceed on two surfaces  $^3A''$  and  $^3A'$  with a difference in barriers of approximately 3 kcal/mole ( $^3A''$  being lower). The  $^3A''$  adduct is predicted to have nearly equal barriers to hydrogen atom dissociation, (2), and hydrogen atom migration (3), both being approximately 8 kcal/mole below the entrance channel barrier. The hydrogen migration transition state is found to be very highly non-planar.

Since the calculations predict the exit channel barriers to be much lower than the entrance channel barrier, all of the  $OHCCH^*$  formed is expected to lead to products via reactions (2) and (3), none should dissociate to reactants, (-1). Thus the total rate of reaction should be equal to the rate of addition, (1). Transition state theory calculations employing the ab initio geometries, frequencies and an adjusted barrier to addition of 2 kcal/mole lead to good agreement with numerous experimental measurements of the total rate of reaction up to 600 K. Above 1500 K, Lohr & Roth have reported separate measurements of both oxygen loss, to obtain a total rate constant, and hydrogen gain, to obtain a rate constant for reaction (2). Comparison between theory and experiment suggests that the measured total rate constant is too high and should in fact be about equal to the measured value of the rate for hydrogen production.

RRKM calculations on the branching ratio for product formation, its temperature dependence, and the lifetime of  $OHCCH^*$  will also be reported. These results will be compared with available thermal and molecular beam measurements.

\*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under Contract W-31-109-Eng-38.

QUASI-CLASSICAL TRAJECTORY STUDY OF COLLISION-INDUCED DISSOCIATION  
IN COLLINEAR ATOM-DIATOMIC MOLECULE COLLISIONS

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The development of the hyperspherical coordinates method for studying collision-induced dissociation (CID) in collinear atom-diatomic molecule collisions has demonstrated that, in general, classical mechanics gives a qualitatively accurate picture of this process, even for very weakly bound systems where quantum effects might be expected to be important. Quasi-classical trajectory analysis has shown that trajectories leading to CID tend to fall in groups (reactivity bands) based on the trajectory's initial phase and energy.

In this work, the effect of variation of the atomic masses and properties of the potential energy surface on dissociation probabilities and partitioning of kinetic energy among the atomic products of CID are considered. Comparison to quantum mechanical calculations, where available, is made. Attention is given to exploring the usefulness of the reactivity band picture of CID. Preliminary results indicate that this picture holds reasonably well under all conditions studied, and that large changes in the atomic masses do not alter the usefulness of classical mechanics for study of CID. Reagent vibrational excitation is seen to lead to enhancement of CID.

Thermochemistry of the Decomposition of Energetic Materials:  
Application of the BAC-MP4 Method\*

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Sandia National Laboratories, Livermore CA 94550

George F. Adams and Byron H. Lengsfeld III  
US Army Ballistic Research Laboratory  
Aberdeen Proving Ground, MD

The thermochemistry (bond energies, heats of formation, and free energies) of molecular species involved in the decomposition of energetic materials used in propellants and explosives has been investigated theoretically using the recently developed quantum chemical BAC-MP4 method (Bond Additivity Corrected Moller-Plesset Fourth Order Perturbation Theory). The BAC-MP4 method provides accurate heats of formation for unstable and radical species occurring in the decomposition process. The method is also used to determine the reaction pathways for molecular rearrangement and decomposition. Results are presented for various nitro- and nitroso- compounds. The importance of radical attack, particularly by H atoms, in the decomposition process is discussed.

\*This work supported by the U. S. Department of Energy and the U. S. Army.

# HOMOGENEOUS EXCHANGE REACTION BETWEEN HYDROGEN AND DEUTERIUM

by Martin J. Rabinowitz and William C. Gardiner, Jr.

Department of Chemistry, University of Texas-Austin,  
Austin, Texas 78712

The isotope exchange reaction between hydrogen and deuterium was studied in incident and reflected shock waves over the temperature range 1200 to 1800 K by vacuum ultraviolet absorption spectroscopy. The observed exchange reaction ensued after long induction periods at rates that proved to account for the amounts of exchange previously seen in single pulse shock tube and reflected wave mass spectrometric investigations. From the absence of detectable reaction during the induction period, lower bounds of 70 and 45 kcal were placed on the barriers to molecular exchange in 4 and 6 center transition structures, respectively.

## Shapes of Activation Barriers for Hydrogen Atom Transfers from Curved Arrhenius Plots

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Chemistry Department  
Dalhousie University  
Halifax, Nova Scotia, Canada B3H 4J3

Expressions for the temperature dependence of the tunnel effect have been fitted by least squares methods to theoretical and experimental curved Arrhenius plots. The expressions describe tunneling in one dimension through parabolic and Eckart activation barriers. The pre-exponential factor, the effective barrier height and the curvature of the barrier top were treated as variable parameters. The theoretical Arrhenius plot, from an accurate, three-dimensional quantum scattering calculation for the reaction of hydrogen atoms with para-hydrogen, was used to test the validity of such fits. The expressions fitted the plot within 9% over wide temperature ranges. The values of the barrier parameters did not depend strongly on the expression or temperature range chosen. However, the effective barrier height was found to be much lower than the height of the three-dimensional barrier used in the original scattering calculations.

Experimental Arrhenius plots for several gas phase, hydrogen transfer reactions have also been fitted to one-dimensional tunneling expressions. The effective heights and curvatures of the barriers corresponding to these fits will be discussed.

Kinetics Controlled Completely by the Reaction Free Energy:  
Entropy Effects and Fast Endothermic Reactions.

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Bureau of Standards, Gaithersburg, MD 20899

Exothermic gas-phase charge transfer and proton transfer reactions usually involve small entropy changes, and the reactions are fast, i.e., the reaction efficiency is usually near unity. However, when large entropy changes occur, it is observed that the kinetics are controlled not by the enthalpy but by the free energy change. Experimental results show that the reaction efficiencies are determined entirely by the overall reaction free energy, and the properties of the transition complex have no effect. These reactions display the following properties:

- the reactions are intrinsically fast, i.e., the sum of the forward and reverse reactions efficiencies is near unity ( $r_f + r_r = 1$ ).

- the reaction efficiency is determined entirely by the overall free energy change, or equilibrium constant, by the simple relation  $r = K / (1+K)$ . This relation is confirmed experimentally for  $r = 0.02$  to 1.

As a special case, reactions endothermic by as much as 5 kcal/mol can still be fast, i. e., proceed near unit efficiency when a positive entropy change renders  $G^\circ$  negative.

The kinetic behavior can be modelled by a mechanism which proceeds through a single well, i.e., a single common reaction intermediate formed from the reactants or products. This intermediate dissociates to the reactants or products according to the equilibrium ratio, in accordance with transition state theory.

# Quantum mechanical tunneling reaction and diffusion of H(D) atoms in solid hydrogen at 4.2 and 1.9 K

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The radiolysis of  $H_2$ ,  $D_2$ , HD, and  $D_2-H_2$  mixtures has been studied at 4.2 and 1.9 K by ESR spectroscopy. Though the amounts of H atoms produced by  $\gamma$ -irradiation of solid  $H_2$  decrease rapidly upon storage of the irradiated samples at 4.2 and 1.9 K, those of D atoms in the  $\gamma$ -irradiated solid  $D_2$  decrease very slowly. The fast decay of the H atoms at the two ultralow temperatures can be explained only by a model of tunneling diffusion. H and D atoms are produced in the radiolysis of solid HD. Though the amounts of the H atoms are nearly constant upon storage of the sample at 4.2 and 1.9 K, the D atoms decay fast at these temperatures. The fast decay of the D atoms in HD is due to the  $HD + D \rightarrow H + D_2$  reaction caused by a quantum mechanical tunneling. The rate constant for this tunneling reaction was obtained experimentally as  $2.3 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 4.2 K and  $2.1 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 1.9 K. In the radiolysis of  $D_2-H_2$  mixtures the yields of trapped D atoms decrease drastically upon addition of a small amount of  $H_2$ , while the yields of trapped H atoms increase complementarily. The remarkable isotope effect on the formation of the D and H atoms is explained in terms of a large difference of the rate constant for the two tunneling reactions:  $H_2 + D$  and  $D_2 + H$  reactions.  $k_{H_2+D}/k_{D_2+H}$  exceeds  $3 \times 10^4$  at 4.2 K. All results in this work can be explained qualitatively by the rate constants for the tunneling reaction calculated by use of an unsymmetrical Eckart potential.

STUDIES OF EQUILIBRIA OF THE REACTIONS OF ALKYL RADICALS WITH  
MOLECULAR OXYGEN

Irene R. Slagle and David Gutman, Department of Chemistry  
Illinois Institute of Technology, Chicago, IL 60616

The equilibria between alkyl free radicals(R) and molecular oxygen,  $R + O_2 \rightleftharpoons RO_2$ , are being studied as a function of temperature to gain new knowledge of the thermochemistry of these important processes. The free radicals are generated homogeneously in a tubular reactor by the UV laser photolysis of suitable precursor molecules. The relaxation of the radicals to equilibrium in the presence of  $O_2$  are monitored in real-time experiments using photoionization mass spectrometry. The experiments yield at least one value of the equilibrium constant at each temperature of the study. Enthalpy changes for these equilibria are being obtained using both Second and Third Law methods. These studies are providing the most direct measurements to data of the enthalpy changes associated with these reactions and hence of the Heat of Formation of the alkylperoxyl radicals that are formed in them. Comparisons between the measured values and calculated ones obtained from group additivity procedures provide a test of group additivity assumptions. For the equilibrium  $i-C_3H_7 + O_2 \rightleftharpoons i-C_3H_7O_2$ , the measured value of  $\Delta H^\circ_{298}$  is  $-37.7 \pm 1.8$  kcal/mole. This is 6 kcal/mole below that obtained from group additivity estimates. Reasons for this disparity based on recent ab initio calculations of the Heats of Formation of  $RO_2$  compounds by Carl Melius will be discussed.



KINETICS AND ENERGETICS OF REACTIONS OF HYDROCARBON  
FREE RADICALS WITH O<sub>2</sub> IN THE GAS PHASE

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Following our previous studies of OH reactions with hydrocarbons and their distribution of primary products we have now begun a systematic investigation of reactions of hydrocarbon free radicals with O<sub>2</sub>. The reactions we have studied include CH<sub>3</sub>O (methoxy), C<sub>2</sub>H<sub>5</sub>O (ethoxy), CH<sub>2</sub>CHO (vinoxy), C<sub>6</sub>H<sub>7</sub> (cyclohexadienyl), and C<sub>6</sub>H<sub>6</sub>OH (hydroxy-cyclohexadienyl). The experimental techniques involve excimer laser photolysis (for the generation of radicals) and LIF or long-path cw-UV-laser absorption (for their time resolved detection).

The main aspects of this work include

- i. the study of the overall kinetics ( $k(p, T)$ ) of these reactions
- ii. the determination of the branching ratio of H atom abstraction (forming HO<sub>2</sub>) and addition (forming the peroxy-compounds)
- iii. the determination of the stability of the O<sub>2</sub> adducts and their subsequent decompositions into other products.

The different reactivities of carbon and oxygen centered radicals as well as the origin of activation barriers of O<sub>2</sub> addition to resonance stabilized radicals will be discussed.

Inverse Laplace transformation of rate data for  $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$

Joanne W. Austin, Nicholas J.B. Green and Michael J. Pilling

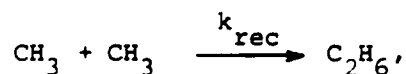
Physical Chemistry Laboratory, South Parks Rd., Oxford OX1 3QZ, U.K.

The inversion of limiting high pressure rate constants for dissociation reactions,  $k_{\text{diss}}^{\infty}$ , to obtain  $k(E)$ , the microcanonical dissociation rate constant, has been discussed by Slater,<sup>1</sup> Forst<sup>2</sup> and Yau and Pritchard<sup>3</sup>:-

$$k(E)N(E) = L^{-1}\{k_{\text{diss}}^{\infty}(T)Q(T)\}, \quad (1)$$

where  $N(E)$  is the rovibrational density of states and  $Q(T)$  the rovibrational partition function for the dissociating molecule. A major limitation in the application of eqn (1) is the difficulty in measuring  $k_{\text{diss}}^{\infty}$  accurately over a wide range of temperatures. Recombination rate constants, on the other hand, can be measured accurately and the comparative invariance of  $k_{\text{rec}}^{\infty}(T)$  with  $T$  allows recombination to be studied over a wide range of temperatures.

We recently reported high precision measurements on the reaction:-



over the temperature range 296-577K and commented on the negative temperature dependence of  $k_{\text{rec}}^{\infty}$ .<sup>4</sup> We have now extended these measurements to higher temperatures and, through an inverse Laplace transformation, obtained  $k(E)$ , the microcanonical rate constant for dissociation of  $\text{C}_2\text{H}_6$ . The experimental data require a significantly slower increase in  $k(E)$  than is obtained by a variational treatment of the dissociation with a Morse potential, a free internal rotor in the transition state and a single parameter,  $\alpha$ , describing the exponential dependence of  $\nu_2$ ,  $\nu_6$ ,  $\nu_9$  and  $\nu_{12}$  on bond distance.

1. N.B. Slater, Proc. Leeds Philos. Lit. Soc., Sci. Sect., 1955, 6, 259.
2. W. Forst, J. Phys. Chem., 1982, 86, 1771.
3. A.W. Yau and H.O. Pritchard, Can. J. Chem., 1979, 57, 2458.
4. M.T. Macpherson, M.J. Pilling and M.J.C. Smith, Chem. Phys. Lett., 1983, 94, 430; J. Phys. Chem., in press.

**AN INTRAMOLECULAR TRANSITION STATE THEORY  
FOR HIGHLY VIBRATIONALLY EXCITED MOLECULES:  
APPLICATION TO A MODEL OF OCS\***

Michael J. Davis and Albert F. Wagner  
Theoretical Chemistry Group  
Chemistry Division  
Argonne National Laboratory  
Argonne, Illinois 60439

For reactions where bonds are broken and new bonds are formed, the concept of reaction bottlenecks (or dividing surfaces or transition states) have been embodied in various forms of transition state theory and RRKM theory with highly successful results. Do such concepts also allow the description intramolecular energy relaxation of molecules initially highly excited in only a few degrees of freedom while the remaining degrees of freedom are initially cold? Such molecules are created in addition and recombination reactions and by photochemical means. If there were severe bottlenecks to energy flow, then this would affect the ability of a molecule to marshall its energy to break a bond. In other words, energy relaxation and reaction dynamics would become strongly coupled. The use of RRKM theory alone implicitly assumes there are no severe bottlenecks to energy relaxation.

Recently MacKay, Meiss, and Percival and Bensimon and Kadanoff have developed a theory of relaxation in terms of bottlenecks and applied it to mathematical constructs exhibiting relaxation. In this poster, the theory is applied for the first time to energy relaxation in molecules. OCS is the molecule studied for which a reasonably accurate potential energy surface is known. For simplicity, the bending degree of freedom is ignored and the molecule is kept collinear. The theory is in the form of an intramolecular transition state theory in which a bottleneck (or dividing surface or transition state) is calculated and the phase space size of that bottleneck relative to the phase space size of molecular configurations on one side of the bottleneck gives the rate of energy relaxation. This rate compares well to the rate determined by classical trajectories, indicating recrossing problems are insignificant. The energy relaxation bottleneck is found to be severe enough to introduce mode specificity in the unimolecular dissociation of collinear OCS.

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\* Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under contract number W-31-109-ENG-38.

## CHEMICAL KINETIC MECHANISMS FOR OXIDATION OF CHLORINATED METHANES

by

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Submitted to

International Conference on Chemical Kinetics  
National Bureau of Standards  
Gaithersburg, Maryland USA  
June 17-19, 1985

The combustion of chlorinated hydrocarbons (CHC) is of interest because of the growing concern for the safe incineration of hazardous materials. There have been no systematic studies on the mechanisms of CHC oxidation at combustion temperatures. This paper will present detailed kinetic mechanisms for the oxidation of chlorinated methanes at elevated temperatures. The mechanisms are composed of elementary chemical reactions whose thermochemical parameters, rate coefficients and equilibrium constants, were primarily taken from established literature sources. Pressure dependencies, whenever necessary, were incorporated following the RRK method of Warnatz. When reaction parameters were not available, they were estimated according to various methods including that of Benson. The analysis of the mechanisms was based on a complete sensitivity analysis. The mechanisms account for the results of shock tube experiments performed over the temperature range 1300-1600 K at a pressure of 2 atm.

KINETIC AND CHEMICAL STUDY OF THE GAS-PHASE  
OXIDATION OF ISOBUTANE AND PROPANE

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The slow oxidations of isobutane and propane at low extents of reaction were studied at subatmospheric pressure in the temperature range 300-350°C, in a static reaction vessel. For each reaction, the major primary products were identified and measured. The predominant product (approximately 60 % of the reaction products, water not included) is the conjugate alkene (isobutene or propene) with substantial yields of a heterocyclic compound (isobutene or propene oxide). Other primary products, especially aldehydes are also formed. For each alkane studied, the reaction products appear very similar.

By studying the possible elementary steps, the reaction channels accounting for the formation of the primary products are put forward and, by using the methods of Thermochemical Kinetics developed by S.W. BENSON and co-workers at Stanford Research Institute <sup>(1)</sup>, the kinetic parameters of most proposed elementary steps are estimated. The numerical values of the rate constants obtained by these methods are quite consistent with our experimental results.

The contributed paper will emphasize the conclusion that these two oxidations can be described by a single reaction mechanism. The only difference consists in the numerical values of the rate constants for the elementary steps.

<sup>(1)</sup> S.W. BENSON - Thermochemical Kinetics, 2nd ed., John Wiley (1976).

COMPUTER PROGRAM FOR THE CALCULATION  
OF THERMOCHEMICAL DATA OF MOLECULES  
AND FREE RADICALS IN THE GAS PHASE,  
AND SECURITY CRITERIA OF CHEMICALS

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A program THERGAS for the automatic computing of thermochemical data of molecules, free radicals, molecular and free radical reactions in the gas phase, based on the methods of Thermochemical Kinetics developed by S.W. BENSON and co-workers, has been set up. The program also computes security criteria for chemicals, as defined by A.S.T.M. (CHETAH program).

For all the above calculations, the program only needs the input of the molecular formula(e) of the compound(s) under study. This input is achieved by means of a linear notation, thus needing no graphic terminal.

The program identifies in a chemical compound BENSON's groups, ring, cis, ortho and gauche corrections, and finds in tables the corresponding data, as well as bond dissociation energies. It computes the external and internal symmetry numbers, the optical isomers numbers, the spin effect. The program achieves a differential vibrational analysis between a given free radical R• and the corresponding model molecule RH, in order to evaluate the terms due to the 3 supplementary degrees of freedom, as well as the possible changes in the values of moments of inertia and potential barriers of some internal rotations.

The outputs are the following :

- $\Delta H_f^\circ$  (300 K)  $S^\circ$  (300 K) and  $C_p^\circ$  (300 to 1500 K)
- $\Delta H_f^\circ$  and  $S^\circ$  for a molecule or a free radical,  $\Delta H^\circ$  and  $\Delta S^\circ$  for a reaction, at any temperature between 300 and 1500 K
- 4 security criteria and corresponding hazard levels for a chemical compound or mixture.

The data base includes around 400 groups made of 20 different atoms and 120 R-H bond dissociation energies.

## Towards an Expert System for Gas Phase Reaction Mechanisms

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In the operation of an expert system a task is assigned to a computer which it proceeds to accomplish on the basis of a set of rules devised by experts in the field. Where there are deficiencies in the rules the system produces a range of possible results which may be compared with experimental findings and, on that basis, further rules may be produced, or the existing ones refined. In this way the system "learns". We describe such a system which is under development for the prediction of isothermal gas-phase reaction mechanisms.

Given the initial conditions (reactant(s), concentrations, temperature) the system generates all of the possible elementary reactions which the reactants and the subsequent radical products can undergo at the various stages in the reaction. A numerical integration programme may then generate product concentrations as a function of time. With all but the smallest of molecules the number of reactions so generated far exceeds the capacity of the computer to perform the integration in an acceptable time. Our system enables the user to test the validity of simple rules which will allow reduction of the complete mechanism of all possible reactions to a manageable size.

In this presentation we demonstrate the approaches we have adopted and progress achieved.



A REEVALUATION OF LOW TEMPERATURE EXPERIMENTAL RATE DATA FOR  
THE REACTIONS OF O ATOMS WITH METHANE, ETHANE, AND NEOPENTANE\*

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The experimental data for the reactions of oxygen atoms with methane, ethane, and neopentane at temperatures below ca. 600 K have been reexamined. In the case of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  reactions, detailed computer models have been assembled to test the assumptions regarding stoichiometries that were made in the original studies in order to derive elementary rate coefficients from the experimentally observed reaction rates. It was found in both cases that the measurements are especially sensitive to secondary reactions not taken into account and impurities in the reagent alkane. Because the original reports did not include sufficient experimental details, it is not now possible to correct their results quantitatively. However, it appears, qualitatively, that the values for the  $\text{O} + \text{CH}_4$  and  $\text{O} + \text{C}_2\text{H}_6$  rate coefficients were overestimated by factors of approximately 2 to 3 in the 250 - 400 K temperature range, with the error increasing as T decreases. Although the experimental results for the  $\text{O} + \text{neopentane}$  reaction are not as sensitive to the same kinds of complications, a comparison of the low temperature measurements with those for the  $\text{O} + \text{ethane}$  reaction suggests that the previously recommended rate coefficients, based on the data of Herron and Huie, are probably also too high by a factor of 2 to 3.

\* Work supported by the National Bureau of Standards under Grant No. NB83-NADA-4034.

# Sensitivity Analysis of Inhomogeneous Chemical Reaction Systems by the Method of Polynomial Approximation

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Recently a polynomial approximation method<sup>1</sup> (PAM) of sensitivity analysis was developed for homogeneous chemical reaction systems. The method is well-suited to large scale kinetic models, especially when an inexpensive scanning of the system sensitivity behavior is desired. The computation speed of PAM is extremely fast, and the major computation effort is proportional only to the number of components in the system, not to the number of parameters. The method is now generalized to non-uniform reaction systems.

For kinetics-diffusion problems the equations of the generalized PAM were (similar in form to those of PAM)

$$\underline{A} \underline{z} = \underline{g},$$

where  $\underline{z}$  = vector of sensitivity coefficients at  $L_a \times L_b$  collocation points  $(x_a, t_b)$  ( $L_a, L_b$ : degrees of interpolation polynomials), and where  $\underline{A}$  and  $\underline{g}$ , both independent of  $\underline{z}$ , contained the input information (i.e., initial and boundary conditions, diffusion constants of chemical species, kinetic mechanism of the reaction system, etc.). The generalized PAM shared the same advantages as offered by PAM (see above). The method was applied to a simple biological kinetic model involving enzymatically active membrane with encouraging results.

1. J.-T. Hwang, Int. J. Chem. Kinet., 15, 959 (1983).

Dynamical Systems: Information from First  
Integrals Using Differential Topology

F. G. Gascon and A. Gonzalez-Lopez

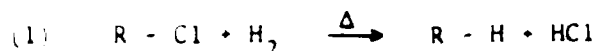
University of Salamanca Dpto. Fisica Teorica  
and  
University Complutense Dpto. Metodos Matematicos  
de la Fisica

The authors show how the knowledge of  $(n-1)$  first integrals (global and or infinite class) in a set of  $n$  first order differential equations leads, assuming that they are globally independent, to a lot of physical information concerning the trajectories of the solutions of the system of differential equations. In particular, even if the system is integrable by quadratures the possibility of trajectories (for  $n \geq 3$ ) of type S and R (simultaneously) cannot be excluded. This is an example of the care, and the lot of information that can be obtained, and importance of relating deep mathematics in questions of differential equations.

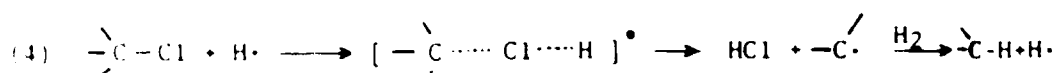
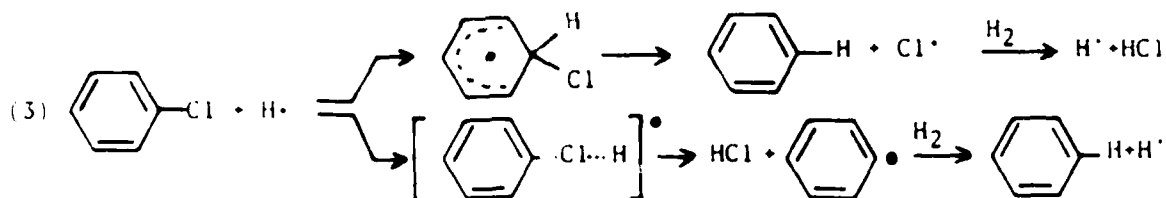
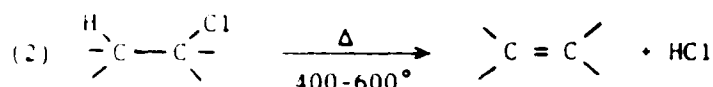
# GAS-PHASE THERMAL HYDROGENOLYSIS OF ORGANIC CHLORINE COMPOUNDS

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Thermal hydro-dechlorination, overall equation (1), is outlined and compared with the behavior of chlorine derivatives in inert atmospheres (pyrolysis), and in air (combustion).



Reaction kinetics and product distributions were studied for various chlorinated compounds, such as (poly)chlorinated benzenes, biphenyls, ethylenes and methanes. With compounds lacking the possibility of molecular  $\beta$ -elimination of HCl (2), dechlorination/formation of HCl proceeds generally between 600-800°C,  $\tau=10$ s, by virtue of free-radical steps such as (3) and (4):



Using a tubular flow reactor, it is observed that at high temperatures complete dechlorination is achieved in a few seconds for a great number of compounds.

Hydrogenolysis is an alternative to high-temperature incineration of industrial wastes. Studies aiming at upscaling and application are in progress.

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# THE STRAINLESS $C-(F)_2(C)_2$ ( $-CF_2-$ ) GROUP AND THE STRAIN ENERGIES OF FLUORINATED CYCLOALKANES

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The strain energy of a species is defined as the difference of its heat of formation and that of a hypothetical species composed of the same groups. For alicyclic hydrocarbons, the groups are  $C-(H)_3(C)$ ,  $C-(H)_2(C)_2$ ,  $C-(H)(C)_3$ , and  $C-(C)_4$ , alternatively recognized as methyl, methylene, methine and quaternary carbon. The strainless group energies are quite easily determined by a variety of techniques and the values are essentially independent of the method used. For example, when that for  $C-(H)_2(C)_2$  is derived "statistically" (à la Benson, Schleyer, Allinger), from "homodesmotic" reasoning [e.g.  $C_3H_8 - C_2H_6$ ,  $1/n((CH_3(CH_2)_nCH_3 - C_2H_6)$ ,  $1/(n-1)((CH_3(CH_2)_nCH_3) - C_3H_8)$ ], or via the "diagonal" approach, i.e. (cyclohexane)/6 or " $1/\infty (CH_2)_\infty$ ", the same value is found within a few tenths of a kcal/mol, -4.93 kcal/mol. By contrast, using the same methods for  $C-(F)_2(C)_2$  give values spread over 10 kcal/mol, from -94.4 to -104.9 kcal/mol. To partially explain this spread and provide a basis for the qualitative and quantitative study of fluorine and organic thermochemistry, three groups  $C-(F)_2(CF_2)_2$ ,  $C-(F)_2(CH_2)_2$  and  $C-(F)_2(CH_2)(CF_2)$  are introduced. It is found that the strain energy of hexafluorocyclopropane is remarkably high, while that of octafluorocyclobutane, likewise low. Implications of these numbers for the understanding fluorinated cycloalkanes and their extrusion reactions, and the nature of strain and aromaticity, will also be discussed.

## The NBS Automated Chemical Kinetics Data Base System

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As part of the continuous NBS activity providing standardized data for use in industry, research and development, the Chemical Kinetics Data Center (CKCD) is involved in compilation and critical evaluation of rate constants and related kinetic parameters of chemical reactions in selected areas. An integrated data base management system has now been developed for fully automated handling and management of chemical kinetic data and associated information. This has required creation of four interrelated Data Bases: CHEM (chemical species), CRNS (chemical reactions), BIBB (bibliography) and JRNS (chemical journals), and development of appropriate Application Programs ("software") for automated formatting, inputting (loading), updating, searching and retrieval of data into and from the four data bases and their cross-referencing. The basic functions of the four data bases are:

DB CHEM serves as a "Directory" of chemical species which appear in chemical reactions as reactants and products. It assures their rapid unambiguous identification through use of "unique identifiers" (an assigned CHEM Access Number for each species, C.A.S. Chemical Name, common Synonyms, C.A.S. Registration Number, Wiswesser Line Notation (WLN), Molecular Formula in a standard Order of Arrangement coupled with an assigned running Isomer Index Number). "Type", "Class" and "Functional Group" Codes are used for rapid selective search and retrieval of specific types, groups and classes of chemical species.

DB CRNS contains information on chemical reactions and the associated data values. Search Codes for chemical reactions are created automatically by the computer from CHEM Access Numbers of the reactants (combined in ascending order) and Type, Class and Functional Group Codes of reactants and products. This arrangement assures a very flexible and rapid selective individual and group search and retrieval of chemical reactions and kinetic data of desired type (experimentally determined literature values, computed values, recommended values, etc.).

DB BIBB contains bibliographic data and allows search by authors, year of publication, journal, etc. DB JRNS contains standard abbreviations and CODENS for chemical journals and assures unambiguous search by journals from DB BIBB.

Necessary Application Programs (software packages) have been developed for automated and integrated handling of data and management of Data Bases. The main features of these programs will be briefly described.

\*Guest Worker

POSTER SESSION B

A COMPARISON OF VARIOUS METHODS  
FOR CALCULATING UNIMOLECULAR REACTION RATE CONSTANTS\*

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For some time, the Rice-Ramsperger-Kassel-Marcus (RRKM) theory of unimolecular reactions has been applied with great success to the calculation of rate constants as a function of energy and to the prediction of the fall-off in rate constant with decreasing pressure [1]. Despite this, revisionists have exhibited renewed interest [2,3,4] during the past few years in various simpler formulations of unimolecular rate constants originally proposed some fifty years ago [5].

In this spirit, rate constants have been calculated using the quantum Kassel model (QRRK) for nine reactions used previously [2,6] as a test for various formulations of unimolecular rate constants. Results obtained are compared with those obtained from RRKM calculations, with those obtained from a model in which the effective number of oscillators ( $s$ ) is related to heat capacity, and with those calculated using a model in which different values of  $s$  are assigned to the reactant molecule and to the activated complex. In addition, a comparison of the QRRK model using an algebraic mean vibrational frequency with that using a geometric mean indicates that the latter is considerably better in fitting the RRKM results.

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\*Research supported by the Division of Chemical Sciences, Office of Basic Energy Research, U.S. Department of Energy.

- [1] Cf., for example, P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Wiley, New York, 1972.
- [2] D. M. Golden, R. K. Solly, and S. W. Benson, J. Phys. Chem. 75, 1333 (1971).
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## DECOMPOSITION OF ALKOXY RADICALS

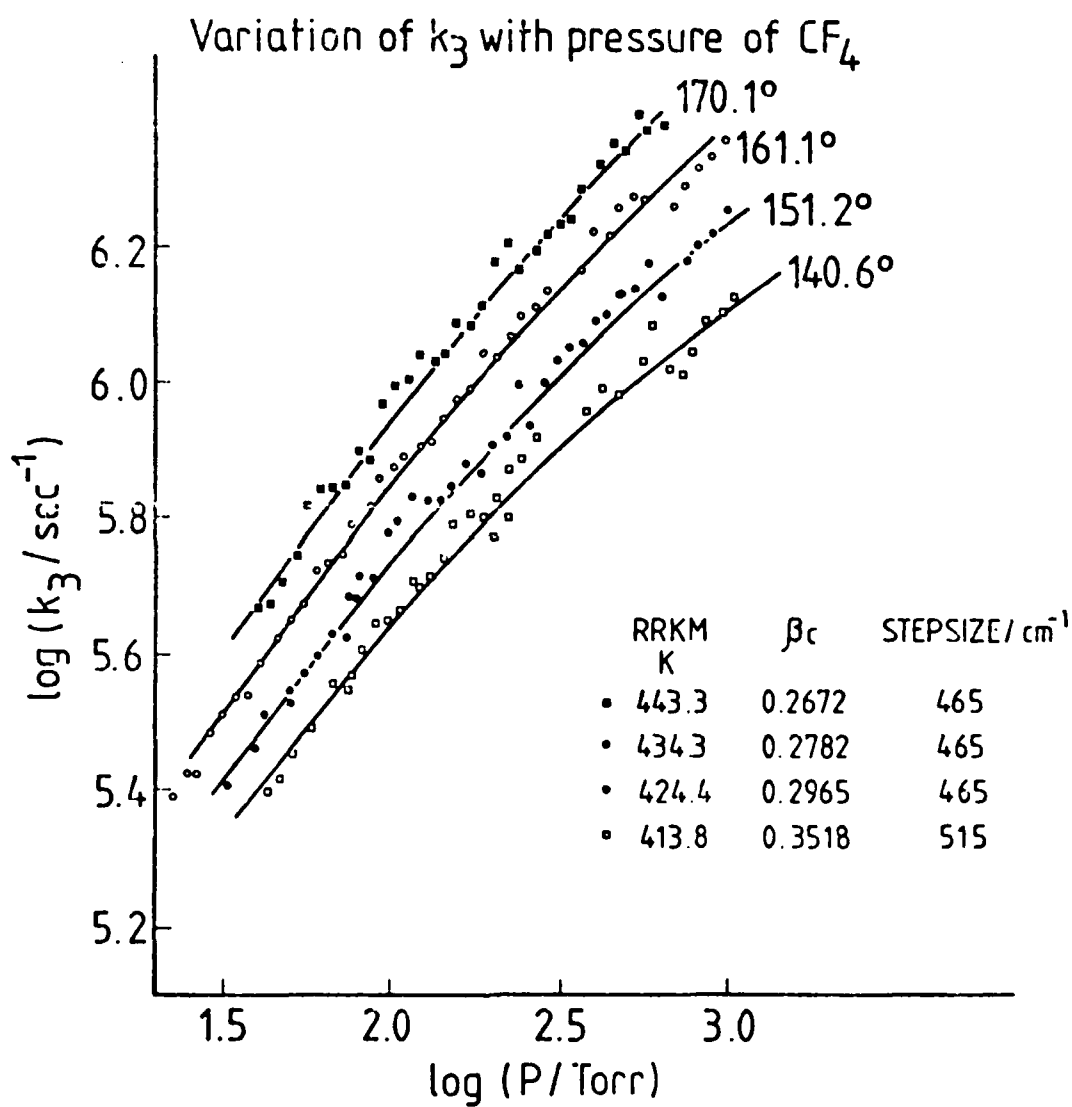
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Studies of the decomposition of alkoxy radicals, both fission and isomerisation, are relevant to both atmospheric chemistry and combustion, and have theoretical implications in terms of the barrier heights for the various possible processes and their RRKM analysis.

For fission processes the values for the rate constants for  $C_1 - C_5$  radicals will be discussed in relation to the Arrhenius parameters with reference to theoretical conclusions, the reverse processes and recent experimental results obtained at Aberdeen. Hydroxy radicals are also included.

Although there is little or no data available for the methoxy radical, because of its importance, the possible decomposition paths including isomerisation, has been the subject of intense theoretical study. For the n-propoxy and n-butoxy radicals, isomerisation appears to be the dominating unimolecular process.

The rate constants of the fission processes for  $CF_3O$ , i-PrO and t-BuO are clearly pressure dependent under the experimental conditions (0-1500 Torr) although that for t-BuO is very close to the high pressure limiting values. In this respect the extrapolation procedure to determine  $k_\infty$  may be critical. We favour the method of plotting  $1/k_{obs}$  versus  $p^{-\alpha}$  ( $0 < \alpha < 1$ ). Excellent fits with theory are obtained for  $CF_3O$ , i-PrO and t-BuO. Results are shown in the figure for t-BuO. However, although admittedly from meagre experimental data, the decomposition of the ethoxy radical shows no pressure dependence at all!

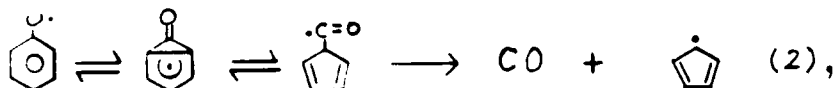


## UNIMOLECULAR DECOMPOSITION OF THE PHENOXY RADICAL IN SHOCK WAVES

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The unimolecular decomposition of the phenoxy radical,  $C_6H_5O \longrightarrow CO + C_5H_5$  (1), is currently believed to be a very important step in the high temperature oxidation of benzene [1-3]. The rate constant for this reaction was first determined by Benson et al. [4] to be  $10 \pm 5 \text{ sec}^{-1}$  at 1000 K. A tentative reaction mechanism,



was also proposed by Benson and co-workers on the basis of a thermochemical kinetic estimate. However, there have been no experimental Arrhenius parameters to support this postulate.

In this study, we have employed a stabilized cw CO laser to probe the CO formation in reaction(1) using a shock tube. Highly diluted mixtures of anisole (0.05-1 % in Ar) were heated with incident shock waves between 1100 and 1400 K at pressures of 0.5-0.9 atm. The rate constant for reaction(1) can be directly calculated from the measured CO concentration profiles according to the first-order kinetic equation,  $k_1 t = \ln(1 - [CO]_t / [\phi O]_0)$ , where  $[\phi O]_0$  is the initial phenoxy radical concentration. A least-square analysis of these data gave rise to  $k_1 = 10^{11.5 \pm 0.4} \exp(-22,500 \pm 1,000/T) \text{ sec}^{-1}$  in the temperature range of 1100-1400 K. The result of a RRKM calculation for this reaction indicated that at temperatures above 1300 K,  $k_1$  becomes slightly pressure-dependent. The extrapolation of the individual data with the RRKM theory led to  $k_1^\infty = 10^{11.8 \pm 0.4} \exp(-23,300 \pm 1,000/T) \text{ sec}^{-1}$ . The low A factor,  $10^{11.8} \text{ sec}^{-1}$ , obtained from this preliminary result supports Benson and co-workers' conclusion that the decomposition of  $C_6H_5O$  takes place via reaction(2) which involves a rather tight activated complex.

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# Pyrolyses of Toluene and Ethylbenzene

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The thermal decompositions of 1.8% toluene and 1.6% ethylbenzene in neon have been investigated in a shock tube coupled to a time-of-flight mass spectrometer over the temperature ranges of 1590-2145 K and 1635-2080 K respectively at 0.3-0.5 atm total pressure. Toluene and ethylbenzene decompose readily at these temperatures forming benzyl radicals and other products. The major products are essentially the same in both cases;  $C_2H_2$ ,  $C_4H_2$ ,  $C_6H_6$  and  $C_6H_2$ . However, substantial amounts of  $CH_4$  and  $C_2H_4$  and small amounts of styrene ( $C_8H_8$ ) are observed in the pyrolysis of ethylbenzene. One most intriguing observation is the growth of  $C_7H_8$  peak, due possibly to the reaction  $C_7H_7 + H \rightarrow C_7H_8$ , in the  $C_8H_{10}$  system.

Reasonable fits to the toluene TOF reaction profiles have been obtained using rate constants from a variety of literature sources. Additionally, the mechanism was used to simulate the ARAS D atom profiles reported by Skinner.<sup>1</sup> The equilibrium constant for the initiation step,  $C_7H_8 = C_7H_7 + H$ , was calculated and the effect of  $k_{-1}$  on the  $C_7H_8$  and  $C_7H_7$  profiles for dilute mixtures was demonstrated using the experimental conditions of Troe.<sup>2</sup> A sensitivity analysis confirmed Skinner's observation that secondary reactions, even under dilute conditions, are important and should not be neglected. The TOF toluene data support initiation primarily via C-H bond rupture to form  $C_7H_7 + H$  rather than C-C split to produce  $C_6H_5 + CH_3$ . However, TOF product analysis of the  $C_8H_{10}$  mixture supports initiation via C-C scission yielding benzyl and methyl radicals.

Lastly, the toluene mechanism is employed to calculate the temperature change in 1.75%  $C_7H_8$  mixture as a function of observation time in a soot yield experiment. The entire soot bell is shifted extensively to lower temperatures when the temperature predicted by the model at a particular observation time is used instead of the no reaction temperature.

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This work is supported by Department of Energy, Contract DE-AS05-79ER10505.

# PYROLYSIS OF ACETYLENE IN A SINGLE-PULSE SHOCK TUBE

by

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Mixtures of acetylene (3.7% and 0.21%) in argon have been pyrolyzed in a single-pulse shock tube. Initial post-shock temperatures varied from approximately 1100 to 2600K, total pressures varied from four to six atmospheres and dwell times ranged from 600 to 800 microseconds. Products have been collected and analyzed using capillary gas chromatography. At elevated temperatures (>1800K) the principal products include hydrogen, diacetylene, and triacetylene. In addition, at concentrations less than 100 ppm, tetracetylene, ethylene, methane, styrene, vinylacetylene, methylacetylene,  $C_6H_4$ , and benzene, were observed. At low temperatures (1100-1300K) the principal product is vinylacetylene with small concentrations of benzene also observed. In the case of these two products, their concentrations peak at approximately 1300 to 1400K and then decrease to steady-state values at the temperatures at which acetylene converts to hydrogen and the di-,tri-, and tetracetylenes.

Chemical kinetic modeling has been undertaken to describe these results. A modification of the shock tube version of the chemkin code has been made to incorporate the effects of quenching characteristic of the single-pulse shock tube. The chemical mechanism for acetylene pyrolysis has been taken from the literature. Good agreement between the experimental and model profiles for acetylene, hydrogen, ethylene, di-,tri- and tetracetylene are obtained. Vinylacetylene is assumed to be formed from the bimolecular reaction  $C_2H_2 + C_2H_2 \rightarrow C_4H_4(l)$ . Excellent quantitative agreement between the observed profile and an expression consistent with low temperature rate measurements of vinylacetylene formation (i.e.,  $k = 1.5 \times 10^{15} \exp(-22,200/T) \text{ cc/mole/sec}$ ) has been obtained.

# HEAT OF FORMATION OF RADICALS FROM SHOCK WAVE PYROLYSIS OF HYDROCARBONS

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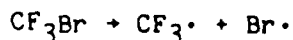
The thermochemistry of vinyl, ethyl and n-propyl radicals has been determined from an investigation of the kinetics of the reactions involved in the pyrolysis of methane, ethylene, propane and 1,3-butadiene behind reflected shock waves from 1400 to 2300K, dependent on the hydrocarbon being studied, at densities of  $(2.5 \text{ to } 4.9) \times 10^{-5}$ . Experimental absorption-time profiles were obtained at 216nm and 239nm from methane and propane pyrolysis and at 239nm from ethylene. The 216nm absorption profile from methane has been corrected for absorption due to vinyl radicals to obtain a pure methyl absorption profile as it has been shown from time-resolved spectroscopy of propane that vinyl has a broad absorption maximum at 239nm and 1350K. From the rate constants obtained by computer modelling the corrected absorption profile of the methyl radical at 216nm and the observed profile at 239nm of the vinyl radical, the following values for the heat of formation at 298K have been established.

Reaction	Radical	$\Delta H_f / \text{kJ mol}^{-1}$
$n\text{-C}_3\text{H}_7 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3$	$n\text{-C}_3\text{H}_7$	$90 \pm 10$
$\text{C}_3\text{H}_8 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_3$	$\text{C}_2\text{H}_5$	$125 \pm 15$
$\text{C}_4\text{H}_6 \rightarrow \text{C}_2\text{H}_3 + \text{C}_2\text{H}_3$	$\text{C}_2\text{H}_3$	$288 \pm 10$
$\text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{H}$	$\text{C}_2\text{H}_3$	$269 \pm 10$
$\text{C}_2\text{H}_4 + \text{H} \rightarrow \text{C}_2\text{H}_3 + \text{H}_2$	$\text{C}_2\text{H}_3$	$273 \pm 10$

# Single Pulse Shock Tube Study on the Stability of Perfluorobromomethane

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Perfluorobromomethane has been decomposed in comparative rate single pulse shock tube experiments. Reaction extent was determined by measuring the ethylene yields from the induced decomposition of cyclopentane. The important processes are



Under our reaction conditions 950-1100K and 2.5-8 atms. the unimolecular decomposition process is clearly in the fall-off region with  $k/k_\infty$  in the .3 to .5 range. The pressure dependence is of the order of  $p^{.37 \pm .05}$ . RRKM calculations that lead to an exact fit of the results yields

$$k_\infty(\text{CF}_3\text{Br} \rightarrow \text{CF}_3\cdot + \text{Br}\cdot) = 10^{15.1} \exp(-34740/T)/\text{sec}.$$

and a step size down of  $6 \pm 2$  kJ with argon as the collisional partner. Failure to observe any effects with cyclopentane concentrations as high as 5% permits an upper limit to be set on the efficiency of a large polyatomic as a collision partner. The high pressure rate expression leads to  $\Delta H_f(\text{CF}_3) = -461.9$  kJ/mol at 300K in satisfactory agreement with existing values and a combination rate of  $\text{CF}_3$  and Br of  $10^{10}$  l/mol-s. This appears to be slower than comparable hydrocarbon systems.

# THE UNIMOLECULAR DISSOCIATION OF TETRAMETHYLDIOXETANE IN THE GAS PHASE

by

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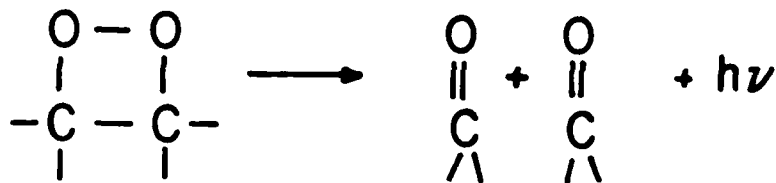
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The unimolecular decomposition of tetramethyldioxetane (TMD) was studied in real time by laser excitation methods.



The reaction rate was followed by monitoring the time resolved chemiluminescence (CL) that ensues. In earlier experiments, Cannon and Crim<sup>(1)</sup> have shown that upon exciting a C-H stretching overtone vibration (to  $v = 4$  or  $5$ ), the molecule dissociates and that the reaction rate can be calculated using a statistical theory (RRKM).

We have used infrared multiphoton excitation (IRMPE) to induce the same reaction<sup>(2-4)</sup>. Assuming that the basic assumption of the statistical theory (namely, complete energy redistribution in excited molecules prior to the reactions) holds also for this method, we were able to estimate the energy distribution of TMD-molecules after IRMPE. This was done by a detailed comparison of the formation and decay kinetics of TMD chemiluminescence induced by the two methods.



The resulting distributions were compared with a calculation based on a rate equation model. It was found that whereas the total yield could be fairly well reconstructed, the calculated distributions differed considerably from the experimental ones for any functional form that allowed the energy dependent absorption cross section to vary smoothly with energy. It was concluded that this simple form of the rate equation model is inadequate in accounting for the IRMPE process.

Analysis of the fluorescence time dependence allowed us to gain insight as to the nature of the excited states leading to the chemiluminescence. We have compared the CL kinetics with those obtained for acetone ( $k_6$  and  $d_6$ ) at low pressures. The acetone study was conducted both in the bulk and in a supersonic nozzle beam expansion. The conclusion is that in the absence of collisions, the species formed by TMD decomposition is a mixed  $n\pi^*$  state of acetone, exhibiting both singlet and triplet character. This state is very rapidly deactivated by collisions, leading primarily to the thermalized triplet. The latter is the state observed in bulk experiments<sup>(5)</sup>.

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## An EPR Study of the Early Stages of TNT Thermal Decomposition

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The mechanism for the thermal decomposition of trinitrotoluene (TNT) has been investigated for over fifty years, yet the initial steps of the reaction are still unknown. Early differential scanning calorimetry results indicated the reaction proceeds via a short induction period ( $E_a = 46.5$  kcal/mol) followed by a post induction reaction ( $E_a = 29.4$  kcal/mol) in which most of the TNT is consumed. These results have been correlated by electron paramagnetic resonance studies of TNT in the condensed phase which show an initial weak radical with considerable fine structure (zero order,  $E_a = 40.9$  kcal/mol) and a later developing intense, broad singlet species (first order,  $E_a = 30.2$  kcal/mol). MNDO studies of TNT indicated a number of different possible reaction mechanisms with calculated activation energies similar to the experimentally observed initial induction step. These possible reactions include the loss of  $\text{NO}_2$ , nitro - nitrite rearrangement, and methyl proton transfer to the nitro group. Stable isotopically labelled analogs of TNT indicated that the EPR couplings observed in the initial radical are due to the para nitrogen and five equivalent (or nearly equivalent) hydrogens. Using  $\alpha\text{-D}_3$  labelled TNT an isotope effect for the post induction period was determined to be 1.7 by DSC and 1.4 by EPR. In an attempt to simplify the complex decomposition mechanism, additional EPR studies were performed with mixtures of TNT and hexamethylbenzene (HMB). Under these conditions the reaction occurs at considerably lower temperatures (150 vs 200 C) and the EPR spectrum is free of the post induction singlet radical species. Several mole fractions of TNT were examined (0.05 to 0.95) to determine the molecularity of the initial reaction. However, EPR spectral identification and kinetic analysis of the first step remain complex. High performance liquid chromatography is now being performed to determine the reaction products.

Gas Phase Unimolecular Dissociation Kinetics of  
Cyclic Perfluoro-Olefins

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Gas phase kinetics for the unimolecular dissociation of cyclic perfluoro-olefins were investigated with the help of a TEA pulsed  $\text{CO}_2$  laser. In these reactions the parent molecule absorbs many photons in rapid succession until the reaction rate becomes comparable to the optical pumping rate.

Decafluorocyclohexene (DFCH) undergoes retro-Diels-Alder reaction and octafluorocyclopentene (OFCP) shows novel five center  $:\text{CF}_2$  elimination.  $:\text{CF}_2$  subsequently recombines to give stable  $\text{C}_2\text{F}_4$ . The evidence for  $\text{CF}_2$  radical formation was obtained by adding a radical scavenger chlorine during irradiation of OFCP;  $\text{CF}_2\text{Cl}_2$  was obtained as a product at the expense of  $\text{CF}_2\text{-CF}_2$ , as detected by gas chromatography. The nascent primary product perfluorobutadiene, formed in highly vibrational excited state in both cases, subsequently isomerises to thermodynamically stable perfluoro cyclobutene.

The effect of added buffer gas has been shown to decrease the dissociation yield. A model is proposed considering collisional deactivation competes with multiphoton dissociation. In case of unfocused laser irradiation of OFCP, the dissociation rate constant  $k(E)$  evaluated from the model calculation is found to decrease exponentially with the increase in added quenchers ( $\text{SF}_6, \text{Ar}$ ). The extrapolated rate constant to zero additive pressure, corresponding to collisionless dissociation of OFCP, was found to be  $9.1 \times 10^6 \text{ Sec}^{-1}$ . But focused laser irradiation of DFCH assuming a 'dog bone' geometry invariably leads to a constant  $k(E)$  as obtained with DFCH/Ar mixtures to be  $1.2 \times 10^7 \text{ Sec}^{-1}$ .

## Laser Powered Homogeneous Pyrolysis of Silane

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The mechanistic details of silane pyrolysis are important both in understanding fundamental aspects of silicon hydride chemistry and in developing growth models for technologically useful thin films. The study of silane pyrolysis has had a long and sometimes controversial history, however. A central issue has been the nature of the primary dissociation step in the homogeneous decomposition. The issue appeared, finally, to have been resolved in favor of a three-center elimination reaction to form silylene and molecular hydrogen with an activation energy of  $\sim 55$  kcal/mole. This mechanistic information has subsequently been used to interpret experiments involving silane decomposition, particularly as a guide in establishing models for thin film growth in silane chemical vapor deposition (CVD).<sup>1,2</sup>

Recently, however, Robertson, Hils and Gallagher (RHG) have presented new silane pyrolysis data under static and flow conditions.<sup>3</sup> They interpret their results in terms of an *exclusively* heterogeneous initiation mechanism giving rise to a chain reaction and exhibiting an activation energy of  $\sim 55$  kcal/mole. They attribute this activation energy to the loss of hydrogen from the growing silicon film. RHG further claim that all previous studies of silane pyrolysis must have involved heterogeneous processes and that the heat of formation of silylene, which is derived from pyrolysis experiments on disilane, is in serious error.

In order to provide further experimental information on the subject, we have studied silane decomposition using infrared laser powered homogeneous pyrolysis (LPHP). The LPHP technique involves using a laser to create a small volume of hot gas in an otherwise ambient temperature reaction vessel. Arrhenius parameters for an unknown reaction may be obtained by comparison of the rate of the unknown reaction with that of a reference reaction, which serves as an internal temperature standard. In this paper we present the results of our study of the LPHP of silane using a TEA-CO<sub>2</sub> laser as the excitation source, SiF<sub>4</sub> as the absorbing gas and cyclopropane isomerization as the internal reference reaction. At a total room temperature pressure of 20 torr we obtain an activation energy for the decomposition of silane of  $52 \pm 7$  kcal/mole. This result strongly supports the claim that there is a homogeneous pathway for silane decomposition with an activation energy in the range

appropriate for the three center elimination and much too low for decomposition to a silyl radical and atomic hydrogen.

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## Laser Powered Homogeneous Pyrolysis of 1,3-Butadiene and 1,3-Vinylacetylene

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Laser Powered Homogeneous Pyrolysis (LPHP) combined with kinetic modeling is used to elucidate the kinetics of 1,3-butadiene ( $1,3\text{-C}_4\text{H}_6$ ) and 1,3-vinylacetylene ( $1,3\text{-C}_4\text{H}_4$ ) pyrolyses, delineating the important reactions in the 800-1500 K temperature region and identifying the important radical species. LPHP using a pulsed  $\text{CO}_2$  laser produces homogeneous, high temperature pyrolyses on the sub-millisecond timescale, restricting the chemistry to a limited set of reactions. In addition to neat pyrolyses, co-reactants ( $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ) are added to probe the important radicals present.

The predominant unimolecular decomposition product of 1,3-butadiene is found to be the vinyl radical,  $\text{C}_2\text{H}_3$ . This is in agreement with recent results by Kiefer<sup>1</sup>, supporting the value of 63.4 kcal/mole for the heat of formation of  $\text{C}_2\text{H}_3$ . The ensuing radical reactions are either hydrogen abstraction to produce the 1,3-butadienyl radical ( $\text{C}_4\text{H}_5$ ) or  $\text{C}_2\text{H}_3$  addition to  $1,3\text{-C}_4\text{H}_6$  to give cyclohexadiene and ultimately  $\text{C}_6\text{H}_6$ . Alternatively, subsequent reaction of  $\text{C}_4\text{H}_5$  with  $\text{C}_2\text{H}_2$  (either produced by the pyrolysis or added to the reactant mixture) also gives  $\text{C}_6\text{H}_6$  as a major product. The rate of  $\text{C}_4\text{H}_5$  addition to  $\text{C}_2\text{H}_2$  compared with  $\text{C}_2\text{H}_3$  addition to  $1,3\text{-C}_4\text{H}_6$  is understood in terms of overall reaction energetics.

A third reaction path explored is Diels-Alder addition of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  to give cyclic products. Under the conditions of pulsed LPHP, no Diels-Alder adducts are observed. While Diels-Alder reactions are expected to occur because of the relatively fast reaction rate constants, the reverse reactions are also fast at these temperatures. Equilibrium calculations confirm that under these low pressure and high temperature conditions, adduct formation is not favored. The lack of evidence for adduct formation or products resulting from adducts implies that their lifetimes are short compared to competing reactions (such as bond cleavage and isomerization). Lower temperature pyrolyses using a cw  $\text{CO}_2$  laser cleanly induce Diels-Alder addition reactions, and measurements on the addition of  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$  to  $1,3\text{-C}_4\text{H}_6$  and  $1,3\text{-C}_4\text{H}_4$  have been made.

<sup>1</sup>J.H. Kiefer, H.C. Wei, R.D. Kern and C.H. Wu, Int. J. Chem. Kinet., submitted for publication.

Primary Process in the Photolysis of Acetaldehyde.

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The photochemistry of acetaldehyde has been extensively studied both with regard to the nature of the primary dissociative processes and the subsequent secondary radical reactions. However, uncertainty still remains concerning the nature and extent of the primary photodissociative reactions. Recent work indicates that the major dissociation pathway occurs from the vibrationally rich first excited triplet state. Since the decay of triplets is controlled to a significant extent by the rate constant for triplet decomposition, triplet lifetime data should provide information on the mechanism and rate constants for triplet state decomposition. The triplet lifetime of acetaldehyde has been determined in the gas phase as a function of temperature and concentration utilising time-resolved laser-excited phosphorescence. The results help to clarify the role of the triplet state in the photodissociative processes.

CORRELATION OF ALKYL AND POLAR  $\alpha$ -SUBSTITUENTS IN THE GAS PHASE  
PYROLYSIS KINETICS OF TERTIARY ALKYL CHLORIDES.

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The kinetics of the gas phase pyrolysis of several  $\alpha$ -alkyl and  $\alpha$ -polar substituents in 2-chloro-2-substituted-propanes were determined in a static system, seasoned with allyl bromide, and in the presence of the chain inhibitors propene and/or toluene. The reactions are homogeneous, unimolecular, and follow a first-order rate law. The results of the present work together with those reported in the literature indicate that  $\alpha$ -alkyl substituents give a very good straight line, when plotting  $\log k/k_0$  versus  $\sigma^*$  values ( $\rho^* = -4.75$ ,  $r = 0.993$ , and intercept = 0.047 at 300°C). However, the  $\log k_{rel.}$  of polar  $\alpha$ -substituents give rise to an inflection point of the line at  $\sigma^*(CH_3) = 0.000$  into another approximate straight line with  $\rho^* = -0.73$ ,  $r = 0.912$  and intercept = -0.194 at 300°C. The present result has been rationalized, as in primary and secondary alkyl chlorides<sup>1,2</sup>, in terms of a slight alteration in the polarity of the transition state due to changes in electronic transmission at the carbon reaction center.

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THE ICN-PAIR MECHANISM THROUGH NEIGHBORING GROUP PARTICIPATION  
IN THE GAS PHASE ELIMINATION KINETICS OF (DIMETHYLAMINO)ALKYL  
ACETATES.

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Científicas (I.V.I.C.), Caracas Venezuela.

The gas phase elimination kinetics of some Dialkylamino esters have been investigated in a static system and in vessels seasoned with allyl bromide. The reactions are homogeneous and unimolecular, follow first-order rate law and are invariable to the presence of a propene inhibitor. The  $(\text{CH}_3)_2\text{N}$  substituent at the alkyl side of some of these acetates appears to provide anchimeric assistance in the elimination; methyl acetate and the corresponding heterocyclic product arise from an intimate ion-pair type of mechanism.

Yields of Molecular Hydrogen in the Elementary  
Reactions  $\text{HO}_2 + \text{HO}_2$  and  $\text{O}(^1\text{D}) + \text{H}_2\text{O}$

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The concentration of molecular hydrogen was measured after photolysis of static mixtures of  $\text{H}_2\text{O}_2$  vapor in 50 torr of  $\text{N}_2$  at 298 K. If the products of the reaction  $\text{HO}_2 + \text{HO}_2$  are considered to be (1)  $\text{H}_2\text{O}_2 + \text{O}_2$  and (2)  $\text{H}_2 + 2\text{O}_2$ , then a branching ratio of  $k_2/k_1 < 0.0022$  was obtained. The branching ratio was obtained by comparing the measured  $\text{H}_2$  concentration with that predicted by a complete photochemical model. For the reaction of  $\text{O}(^1\text{D})$  with  $\text{H}_2\text{O}$  the products are thought to be (3)  $2\text{OH}$  and (4)  $\text{H}_2 + \text{O}_2$ . The hydrogen concentration was measured after photolysis of ozone in excess water vapor. A value for  $k_4/k_3 = 0.006(+0.007, -0.006)$  was obtained at 298 K and 15 torr total pressure. The results are compared with those of other workers.

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INTERNATIONAL CONFERENCE ON CHEMICAL KINETICS PROGRAM  
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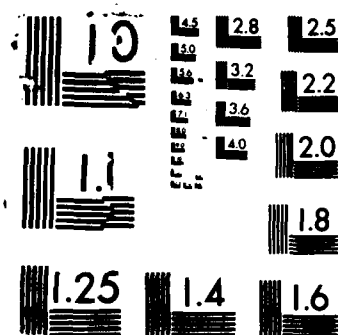
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The Pressure Dependence of the Rate Constants  
for the Reactions  $\text{HO}_2 + \text{HO}_2$  and  
 $\text{HO}_2 + \text{NO}_2 + \text{M}$  at 298K

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The technique of flash photolysis kinetic absorption spectroscopy has been used to investigate the effects of added  $\text{N}_2$  and  $\text{O}_2$  on the rate constants for the reactions:



Measurements were conducted at 298K at total pressures between 25-600 torr.

The results for reaction (1) support the body of recent laboratory data which indicate the existence of both a bimolecular and pressure dependent component for  $k_1$ . An analysis of our combined  $\text{N}_2$  and  $\text{O}_2$  data base results in a rate constant recommendation in air at 298K of

$$k_1 = 1.88 \times 10^{-12} + 5.25 \times 10^{-32} [\text{M}]$$

in molecular units. Our assessment of 95% confidence limits can be best represented by a  $\pm 20\%$  error band. This work additionally indicates a high potential for systematic error in the mathematical analysis of second order decay curves.

The measurements of  $k_2$  are restricted to conditions under which the contribution to the  $\text{HO}_2$  decays from reaction (1) are minimized. At the lowest pressures, however, this second order component is not negligible and is accounted for in the mathematical analysis from a knowledge of initial  $[\text{HO}_2]$ . Careful attention also has to be paid to the potential interference from reaction (3)



where NO is produced via  $\text{NO}_2$  photolysis. Our 298K data for  $\text{N}_2$  and  $\text{O}_2$  between 25-600 torr can be fit to the equation

$$k(M) = \{k_{O,M}[M]/(1 + k_{O,M}[M]/k_\infty)\} 0.6^{1/\alpha}$$

$$\text{where } \alpha = 1 + \{\log(k_{O,M}[M]/k_\infty)\}^2$$

This analysis yields (in molecular units)

$$k_{O,\text{N}_2} = 1.5 \times 10^{-31}$$

$$k_{O,\text{O}_2} = 1.3 \times 10^{-31}$$

$$k_\infty = 5.5 \times 10^{-12}$$

For this reaction system we have assigned a  $\pm 25\%$  error band as representative of 95% confidence limits.

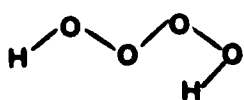
"The IR Spectra, Geometry, and Kinetics of the Dimer  
of HO<sub>2</sub> Radical"\*

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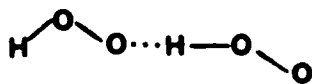
Our recent experimental studies on the matrix/in-situ photolysis preparation and IR spectroscopic characterization of the "H<sub>2</sub>O<sub>4</sub>" species have shown that the dimerization of HO<sub>2</sub> radicals gives a stable, doubly hydrogen-bonded, cyclic species, (HO<sub>2</sub>)<sub>2</sub>.<sup>1-2</sup> The recent gas phase kinetic studies on the self-reaction of HO<sub>2</sub> revealed that the pressure and temperature dependence of the bimolecular rate constant is consistent with the mechanism in which an intermediate with the lifetime in the order of 10<sup>-6</sup> sec. Recent ab initio calculations have shown that open-



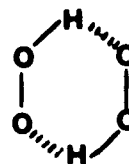
chain isomers and cyclic isomers have comparable binding ener-



(I)



(II)



(III)

gies. The evidence in favor of the cyclic (HO<sub>2</sub>)<sub>2</sub> isomer (III) as the viable "H<sub>2</sub>O<sub>4</sub>" intermediate will be presented.

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4. Private communication of the work by C.F. Melius, J.S. Binkley, and M. Frisch.

\* This research has been supported by NSF grants.

Reactions of  $\text{HO}_2$  with Free Radicals

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The rates of abstraction of H atoms from  $\text{HO}_2$  by other free radicals have unusually large A factors. Also, some of these reactions exhibit strong pressure dependences and negative temperature dependences. To explain these effects it has been suggested that these reactions proceed via an intermediate complex. This paper will present the results of RRKM calculations of rate constants, as a function of temperature and pressure, of the reactions of  $\text{HO}_2$  with a series of free radicals.

Two different models of the intermediate will be considered. The first is the chemically bound molecule,  $\text{HOOR}$ , which can decompose to  $\text{HR}$  and  $\text{O}_2$  via a four center elimination. This model predicts a large negative activation energy (roughly  $-1.5 \text{ kcal mol}^{-1}$ ) and a strong pressure dependence. The second model assumes a hydrogen bonded intermediate; this predicts much weaker pressure and temperature dependences.

The different temperature and pressure dependences should provide a basis for experimentally distinguishing between these two models. The results of the calculations will be used to identify the experiments showing the most promise for this purpose.



Radiative Association:  $A^- + B \rightarrow AB^- + h\nu$ , at 0.1 to 1 torr

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Several systems have been studied in the AFGL selected ion flow tube in which radiative association appears to be occurring. The second order rate coefficients for these reactions vary linearly with pressure and show non-zero intercepts. This indicates that both second order and third order components are present due to radiative association and collisional association, respectively. In some of the systems studied, the measurements were made on a particular reaction in several buffers, and the same intercept was found but with different slopes showing that the non-zero intercept is not an artifact. The systems studied include  $Br^- + WF_6$ ,  $PO_3^- + HCl$ ,  $F^- + BF_3$ ,  $Cl^- + BCl_3$ , and  $Br^- + BCl_3$ . The temperature and pressure dependences of these reactions are reported here. The bond strength for each of these systems is large, on the order of 2 eV or larger. This large bond strength leads to long complex lifetimes, approaching  $10^{-7}$  s for  $(Br^-WF_6)^*$ . Large radiative rates coefficients on the order of  $10^5$  to  $10^7$  s $^{-1}$  are inferred, indicating the occurrence of electronic transitions. The reaction of  $Br^-$  with  $WF_6$  also shows a charge transfer component, so that radiative association, collisional association, and charge transfer all compete with each other. The experimental results are compared to statistical theory.

## A Closer Look at Radical Addition Reactions

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Accurate kinetic models of hydrocarbon systems require detailed knowledge of the temperature and pressure dependence for the addition reactions of radicals to unsaturates. It is generally not adequate to assume these reactions are in the high pressure limit. Since these reactions are similar to recombinations in that a long-lived complex can be formed, they can be treated in a similar fashion. Detailed calculations using chemical activation distribution functions and QRRK methods suggest that the chemistry of many of these radical addition systems changes dramatically with increases in temperature. For example, in  $\text{CH}_3$  addition the energy of the collision complex rises rapidly with temperature and there is soon ample energy to access the C-H  $\beta$  scission channel to form a higher molecular weight olefin and H atoms. The branching rate of stabilization to higher olefin + H is a sensitive function of both temperature and pressure. Even more dramatic behavior is predicted for reactions of  $\text{C}_2\text{H}_3$ ,  $\text{C}_2\text{H}$  and  $\text{C}_4\text{H}_5$  since the barriers to C-H  $\beta$  scission here are comparable ( $\text{C}_2\text{H}_3$ ,  $\text{C}_4\text{H}_5$ ) or lower ( $\text{C}_2\text{H}$ ) than the barrier for the reverse of the addition reaction. As a result, the falloff region persists to even lower temperatures.

This approach has also been extended to include isomerization of the energized complex. One particularly interesting aspect here is the possibility of 1, 3 H shifts in the energized complex since much, if not all, of the energy required to surmount this barrier may already be present.

Generic A-factors for decomposition of the various complexes have been obtained by analysis of a number of recombination and addition rates and the appropriate equilibrium constants. With these values, it becomes a simple exercise to calculate appropriate rate constants in these system as functions of temperature and pressure. Comparisons of several of these calculations to existing literature values suggest that this approach provides a reliable estimate of rate constants; these can then be incorporated into detailed kinetic models which span appreciable temperature and pressure ranges.

# Direct observation of equilibration in $\text{H} + \text{C}_2\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_5$

Phillip D. Lightfoot, Mark Brouard and Michael J. Pilling

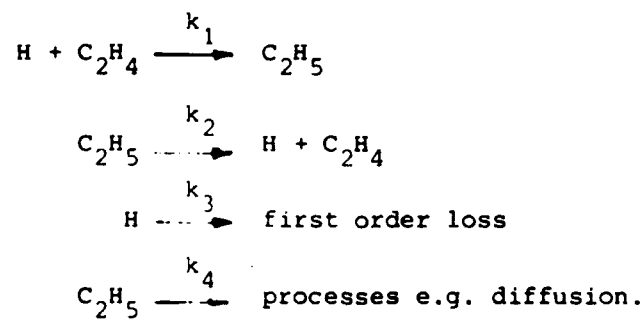
Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ.

The reaction between H and  $\text{C}_2\text{H}_4$ , in a helium diluent, has been studied over the temperature range 285-800K, and at pressures of 50-700 Torr, using ArF laser photolysis and resonance fluorescence. At the lower temperatures ( $T < 600$ ) fall-off fits using the Troe factorisation procedure produces parameters for the evaluation of the rate constant as a function of P and T. The  $k_{\infty}(T)$  values, when combined with those of Lee et al<sup>1</sup>, give:-

$$k_{\infty}(T) = (3.98 \pm 0.44) \times 10^{-11} \exp\{-(1065 \pm 30)/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

for  $200 < T < 600\text{K}$  (uncertainties:  $\pm 2\%$ ).

For  $T > 750\text{K}$ , the H atom decay becomes bi-exponential as the product radical,  $\text{C}_2\text{H}_5$ , begins to dissociate on the timescale of its formation. The data respond well to an analysis based on the kinetic scheme:



The measurement of  $k_1$  and  $k_2$ , under identical conditions, enables the equilibrium constant,  $K_{12}$ , to be evaluated, whilst the pressure dependence of both  $k_1$  and  $k_2$  can be determined directly.

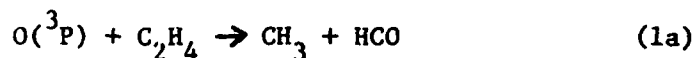
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# HYDROGEN ATOM PRODUCT IN THE REACTION OF GROUND STATE ATOMIC OXYGEN WITH ETHYLENE \*

by

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There is general agreement that the reaction of  $O(^3P)$  with  $C_2H_4$  proceeds via the initial formation of an adduct,  $(C_2H_4O)$ , that is energetically hot.<sup>1,2</sup> However, at ambient temperatures and nominal pressures in the gas phase, the adduct is apparently not stabilized but undergoes decomposition (either trivially back to reactants, or) to products through one or more of the possible exothermic channels:



A wide variety of experimental techniques have been brought to bear on the determination of the product distribution of this important reaction,<sup>1-6</sup> yet to date a clear and definitive consensus has been elusive.

In the present study, the flash photolysis - resonance fluorescence technique was utilized to monitor the formation of the atomic hydrogen product from this reaction. The presumption here is that the H-atom yield provides a measure of the branching ratio for channel (1b),  $\alpha_{1b}$ . And, since it appears that the products are distributed primarily between channels (1a) and (1b), i.e.,  $\alpha_{1a} + \alpha_{1b} = 1$ , this would give the product yield for channel (1a) also.

\* This work was supported by the Chemical Sciences Division, U. S. Department of Energy, Washington, D.C. 20545 undercontract # AC02-76CH00016.

In order to quantify the data obtained in this work, the H-atom product yield was determined relative to the extent of O-atom loss (depletion) by reaction. To do this, it was necessary to perform a relative calibration of the detection system using a gas mixture consisting of  $O_2$ ,  $H_2$ , and helium buffer gas. This relative calibration has been described in the literature.<sup>7</sup> After performing the relative calibration, the signal strengths of both O-atom and H-atom were determined for nominal "reaction" mixtures of  $O_2$ ,  $C_2H_4$ , and argon buffer gas. The determination of the initial relative O-atom concentration was obtained directly from an extrapolation of the atom decay (simple first order exponential) to zero time. The analysis of the H-atom profiles was more complicated, however, and involved fitting the profiles with a computer simulation of a kinetic mechanism which incorporated both formation and loss reactions.

The results of several individual runs at 298K using both the direct relative calibration described above and an indirect calibration give a product yield for H-atom relative to O-atom consumption of about 0.3 to 1.0. This implies that the branching ratio for channel (1b) is  $\alpha_{1b} \sim 0.3$  and thus that  $\alpha_{1a} \sim 0.7$ .

Complete details will be given for the relative calibrations, experimental "reaction" atom profile determinations, and the data analysis. Also, a comparison of this result with those of previous studies will be presented.

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Picosecond Laser Studies of Collisionless UV Photodissociation  
of Gaseous Nitro-compounds

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Picosecond laser UV-photolysis of aliphatic nitroalkanes  $R-NO_2$  and dimethylnitramine (DMNA) has been investigated through laser-induced fluorescence of the  $NO_2$  fragment. Measurements of relative yields and picosecond kinetics are reported for collisionless formation of  $NO_2$ .

Summary:

The study of the initial processes in the collisionless UV photodissociation of nitrocompounds is of importance to identify the chemical intermediates and the reactions involved in the thermal decomposition of energetic materials, even though high temperature and high pressure conditions are normally required in the latter. In the present experiment, UV photolysis of nitrocompounds is investigated by laser excitation at 266 nm of aliphatic nitroalkanes  $RNO_2$  in the  $\pi \leftarrow n$  transition and dimethylnitramine  $(CH_3)_2N-NO_2$  in the  $\pi \leftarrow \pi$  transition.

A single picosecond infrared laser pulse is delivered by a 10 Hz Nd-YAG laser. Amplification and frequency doubling give a 532nm pulse with a 39 ps duration (fwhm) which is further frequency doubled to provide the photolyzing laser pulse at 266nm. The green pulse is then retarded via an optical delay line to probe the  $NO_2$  fragment via laser induced fluorescence (LIF). The two laser pulses are recombined and focused slightly in the T-shaped sample cell containing the nitro compounds at a pressure of 0.1 - 2 Torr. The emitted  $NO_2$  fluorescence is collected at 90 degrees with respect to the laser beams and filtered with two band-pass filters ( $\lambda > 560nm$ ). The signal from a Hamamatsu R928 photomultiplier is averaged with a boxcar integrator (Fig. 1). The zero delay time between the pulses is given by rhodamine 6G photobleaching induced at 266nm.

The main conclusions are the following:

- \* The 266nm excitation of nitromethane leads to its photodissociation and the  $NO_2$  fragment is mainly formed in its ground electronic state (the fraction of electronically excited  $NO_2$  does not exceed  $5 \times 10^{-5}$  in the present experiment), confirming previous literature results(1). The photodissociation is monophotonic.
- \* The quantum efficiency of  $NO_2$  formation does not depend on the nature of the alkyl group ( $R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7$ ).

- \* The kinetics of the  $\text{NO}_2$  formation shows a fast component which fits closely the rhodamine 6G photobleaching and a slow component which extends over  $t=300\text{ps}$  (Fig. 2). We are presently undertaking further experiments to elucidate the nature of the excited states involved.
- \* The dimethylnitramine UV photodissociation at 266nm is more efficient than that of nitroalkanes. After correction for the 266nm absorption cross sections(2), and making the courageous hypothesis that the 532nm absorption cross-section of the  $\text{NO}_2$  fragment is the same in all these experiments, we find that the photodissociation quantum efficiency is four times higher in DMNA. This difference may be related to the smaller dissociation energy of the  $\text{N-NO}_2$  bond (46.2 Kcal/Mol) than the  $\text{C-NO}_2$  bond (58.9 Kcal/Mol). The different electronic states  $\pi \rightarrow n$  and  $\pi \rightarrow \pi^*$  could also play a role.

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2. Herb Nelson and Jimmie McDonald (private communication of the dimethylnitramine absorption spectrum).

This work was performed under contract number 84/819 of the Direction des Recherches, Etudes et Techniques (DRET) (France). J. C. Mialocq is on leave of absence from Centre d'Etudes Nucléaires de Saclay, 91191 Gif-sur-Yvette (France).

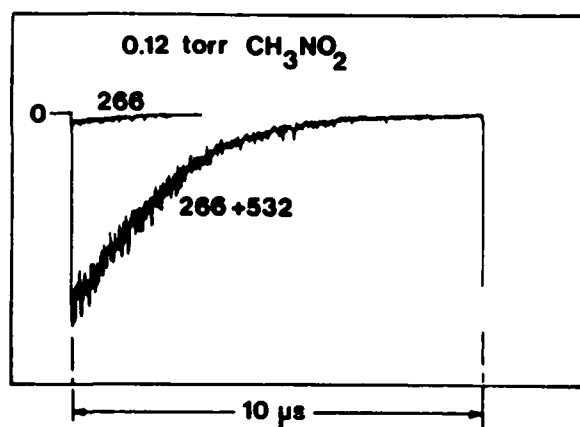


Figure 1.

$\text{NO}_2$  fluorescence as a function of time. The green pulse is delayed by 300ps with respect to the UV pulse.

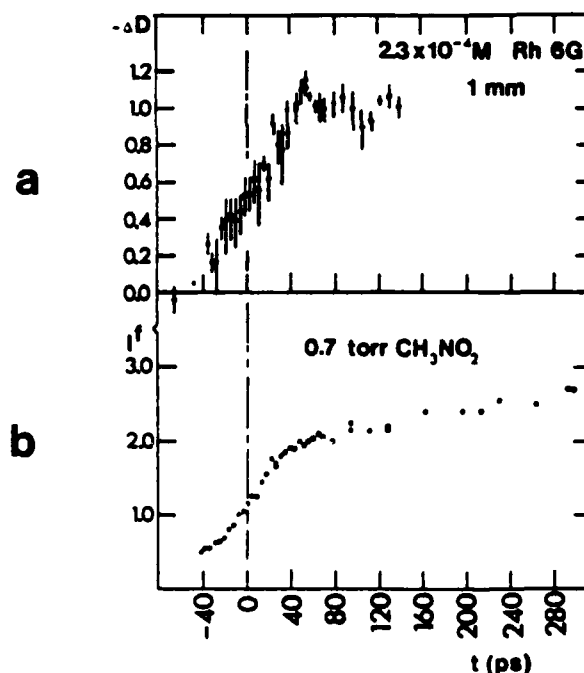


Figure 2.

- a) Photobleaching of Rhodamine 6G at 532nm.
- b) LiF signal, as a function of the delay time of the green pulse with respect to the UV pulse.

The Thermal Decomposition of  $S_2F_{10}$ 

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Chemical Kinetics Division

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The thermal decomposition of  $S_2F_{10}$  was studied by Trost and McIntosh. Subsequently, Benson and Bott reinterpreted the data in terms of the reaction mechanism:



where  $SF_5$  is in equilibrium with  $S_2F_{10}$  and reaction (2) is rate limiting.

In the light of new thermochemical data, it is concluded that reaction (1) is rate limiting. The results of modeling studies of the neat and NO catalysed decomposition of  $S_2F_{10}$  will be presented and the implications for the thermochemistry of  $S_2F_{10}$  and  $SF_4$  discussed.



POSTER SESSION C

## TEMPERATURE DEPENDENCE OF COLLISIONAL ENERGY TRANSFER

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Canada G1K 7P4

Two possible ways for obtaining experimental information about vibrational-to-translational (V-T) energy transfer and its temperature dependence are vibrational relaxation experiments in the absence of reaction ("pure" relaxation), and rate constant measurements in the presence of a heat bath ("weak collision" rates). A very simple analysis of these results is proposed, based on the master equation approach. Given the relative crudeness of the model, only significant trends over a wide temperature range (several thousand  $^{\circ}\text{K}$ ) can be expected to be discerned, which limits the available experimental data to essentially shock tube results. This further limits the choice of experimental subjects to small molecules and monoatomic heat bath gases. Thus unavoidably the sample chosen for analysis is biased both as to the choice of experimental technique and the size of molecules considered, a limitation that should be kept in mind. It turns out that, quite generally, "pure" relaxation and "weak collision" rate constant measurements each examine a different subset of molecules which differ in their average energy content and therefore yield results that are not directly comparable insofar as the V-T energy transfer is concerned. Calculation will be presented based on a suitably modified exponential model of the collisional transition probability that approximate experimental trends.

THEORY OF COLLISIONAL ENERGY TRANSFER DATA OBTAINED FROM  
HIGH-OVERTONE SPECTROSCOPY

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Information on collisional energy transfer between a highly vibrationally excited molecule and a bath gas is important in the study of unimolecular and termolecular reactions. One wishes to find  $P(E, E')$  [the probability that a molecule with initial internal energy  $E'$ , will have a final internal energy  $E$ , after undergoing collision with another molecule] or its first moment ( $\langle \Delta E \rangle$ , the average energy transferred per collision). Recently, Rossi, Pladziewicz and Barker [J. Chem. Phys. (1983) 78 6695] and Hippler and Troe (to be published) have studied the deactivation of highly vibrationally excited azulene molecules by collision with argon atoms using high-overtone spectroscopy. The results of Barker et al. would suggest that the amount of energy transferred per collision depends on the initial internal energy of the azulene molecule; however, the more recent data of Hippler and Troe show no such dependence. An *a priori* calculation of  $P(E, E')$  for this system has been carried out, based on an extension of Gilbert's "biased random walk" model [J. Chem. Phys. 80, 5501 (1984)]. The model assumes that energy migration during the collision is random, except for certain microcanonical statistical constraints; we show that one can then obtain  $P(E, E')$  from a comparatively small number of trajectories using a generalized Langevin equation approach. By calculating trajectories for the azulene/Ar system, employing realistic inter- and intramolecular potentials, we obtain results that are in good accord with the experiments of Hippler and Troe. This suggests that the extended model may be reliably and economically used to calculate appropriate energy transfer quantities.

VIBRATIONAL EXCITATION OF SMALL POLYATOMIC MOLECULES  
BY ENERGY TRANSFER FROM HOT HYDROGEN ATOMS\*

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Brookhaven National Laboratory  
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and

George W. Flynn  
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Columbia University  
New York, NY 10027

Excimer laser photolysis of hydrogen halides or  $\text{H}_2\text{S}$  provides a convenient method for the production of translationally energetic H atoms on a time scale that is instantaneous compared with subsequent collisional processes. Collisions may result in thermalization of the hot atoms, vibrational-rotational excitation of molecular collision partners, or chemical reaction with the collision partners. All of these processes have been monitored in real time using infrared emission from vibrationally-rotationally excited molecules, infrared diode laser absorption, or laser-induced fluorescence in the visible-ultraviolet spectral region.

The vibrational excitation of carbon dioxide, methyl fluoride, and isotopic methanes will be discussed, and the experimental results will be compared with various models for collisional energy transfer. Also, an investigation of the energy disposal and dynamics of the reaction  $\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$  will be described.

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\*Research carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. Support to G. W. Flynn was provided under Department of Energy Contract DE-AC02-78ER04940.

ENERGY TRANSFER IN NON-REACTIVE  $H_2 + OH$  COLLISIONS

2

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 Berkeley, California 94720

We have used the methods of quasi-classical dynamics to compute energy transfer properties of non-reactive  $H_2 + OH$  collisions. The potential energy surface used was the Schatz-Elgersma fit to the ab initio Walsh-Dunning surface. At the end of each trajectory, the final translational energy, rotational energy of each molecule, vibrational energy of each molecule, rotational and vibrational quantum number for each molecule, orbital angular momentum, and scattering angle were determined. Energy transfer has been investigated as a function of translational temperature, reagent rotational energy, and reagent vibrational energy.

The energy transfer mechanism is complex with ten types of energy transfer possible. Evidence was found for all kinds of energy transfer, indicating that energy transfer in diatom-diatom collisions is far more complicated than  $A + BC$  collisions. There is much more exchange between the translational degree of freedom and  $H_2$  vibration than there is between translation and  $OH$  vibration. Translational energy is transferred to the rotational degrees of freedom of each molecule, and the transfer is more favorable for  $OH$  than  $H_2$ . Energy transfer does not depend strongly on the initial angular momentum in either molecule. Vibrational energy is transferred to translation, to the rotational degree of freedom of the same molecule, and to the rotational and vibrational degrees of freedom of the other molecule.  $OH$  does not transfer vibrational energy as effectively as  $H_2$ .

2

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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Science, Chemical Sciences Division of the U.S. Department of Energy under Contract No DE-AC-03-76SF00098.

Product State Distributions in the Vibrational  
Predissociation of the NO-Ethylene and  
NO-Ar Van Der Waals Molecules

D. S King and J. C. Stephenson

National Bureau of Standards

Laser excited fluorescence techniques, including polarization and Doppler spectroscopy have been applied to the determination of the rotational and kinetic energy distributions of the fragments formed from the vibrational predissociation of NO-ethylene following both excitation of the  $\nu_7$  ethylene-like mode at 10 microns and the NO vibration at 5 microns and of NO-Ar following 5 micron excitation. These results also imply lifetimes of these vibrationally excited van der Waals species to be longer than 10 picoseconds.

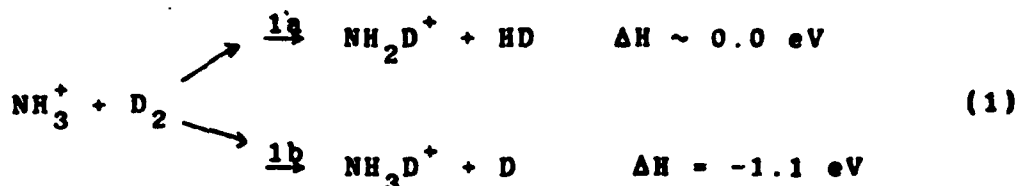
## INTERNAL ENERGY IN ION-MOLECULE REACTIONS:



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Santa Barbara, California 93106

The  $\text{NH}_3^+ + \text{D}_2$  reaction (1) has been studied using Tandem Ion Cyclotron Resonance Spectrometry (TICR).



The analogous  $\text{ND}_3^+ + \text{H}_2$  reaction was also investigated. Using TICR the  $\text{NH}_3^+$  reactant ions are produced, either by electron impact or chemical ionization, in a separate, differentially pumped ion source. The ions are extracted, mass selected and injected into a drift ICR cell where the reaction with  $\text{D}_2$  occurs. The  $\text{NH}_3^+$  injection energy is  $\sim 0.5$  eV (LAB) or  $<0.1$  eV (CM). Different charge transfer reactions can be used to produce  $\text{NH}_3^+$  ions with known amounts of internal energy ranging between 1.0 and 5.0 eV [1]. Thus, the effect of  $\text{NH}_3^+$  internal energy on Reaction 1 can be quantitatively determined. The effect of  $\text{NH}_3^+$  kinetic energy can also be studied using ICR double resonance.

Changing the  $\text{NH}_3^+$  internal energy greatly affects both the total reaction rate and the product distribution of Reaction 1. The ratio of the H-D exchange product (1a) to the Deuterium abstraction product (1b) increases from  $<0.5$  with 1.0 eV internal energy to 11.5 with 5.0 eV internal energy. The total rate coefficient increases by a factor of 6 over the same range. In contrast, increasing the  $\text{NH}_3^+$  kinetic energy from  $\sim 0.1$  eV to  $\sim 2$  eV (CM) causes the same ratio to decline by a factor of 10.

These results are in excellent qualitative agreement with the work of Zare and coworkers [2] in which vibrationally state selected  $\text{NH}_3^+$  ions are reacted with  $\text{D}_2$  at kinetic energies between 1 and 10 eV (CM).

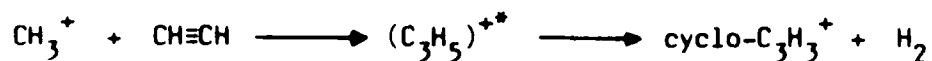
1. P. Kemper, M. Bowers, D. Parent, G. Mauclaire, R. Deraï and R. Marx, J. Chem. Phys. **79** 160 (1983).
2. R.N. Zare, private communication.

**A Study of the Formation of Cyclo-C<sub>3</sub>H<sub>3</sub><sup>+</sup> and Cyclo-C<sub>7</sub>H<sub>7</sub><sup>+</sup>  
in the Gas Phase using a Triple Quadrupole Mass Spectrometer**

J. M. Tedder

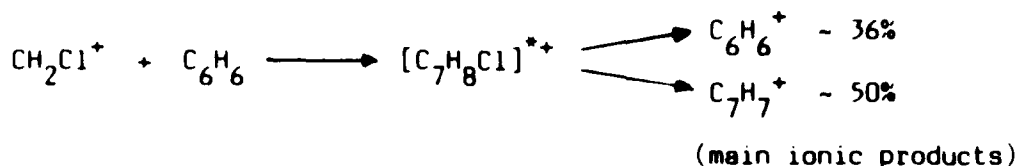
University of St. Andrews, Scotland

The reaction of methyl cations with acetylene occurs at a very high cross section:



The effect of substituents in both the initial carbo-cation and the acetylene has been investigated.

The reaction of methyl and substituted methyl cations with benzene and substituted benzenes has been investigated, e.g.



The effect of the structure of the primary ion and its translational energy on the course of these reactions will be discussed.

The study of ion-molecule reactions using multiple quadrupole mass spectrometers will be discussed and the advantages and disadvantages of the technique will be emphasised.



Radiative Lifetimes and Reaction Rates of Metastable Electronic States in Small Molecular Ions

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The radiative decay rates and reactivities of ionic metastable electronic states have been of interest to the ion chemist since the early days of ion-beam reaction studies. Due to the usually violent methods of production, reactant ions are often formed in a number of electronic states - some of which may persist for long periods of time. The measurement of lifetimes and quenching rates for such states is of importance in evaluating the chemical roles such states play in ion-molecule reactions. We have characterized the radiative decay rates of several molecular ion metastable electronic states using Fourier Transform Mass Spectroscopy to probe reactions which are competitive with unimolecular deactivation. Under the ultra-high vacuum conditions employed ( $p < 10^{-8}$  Torr) the primary deactivation mechanism is typically radiative relaxation. Thus the study of ion loss rates using competitive reactions provides the natural lifetime as well as the reaction rate of the metastable level. Lifetimes and reaction rates of several metastable ions such as  $\text{NO}^+$  and  $\text{O}_2^+$  will be discussed.

Comparison Between the Mechanisms for the Formation of  
Electronically Excited Lead Oxide During the Reaction Between  
Lead Vapor and Either  $^3\Sigma O_2$  or  $^1\Delta O_2$

By

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The kinetic processes leading to the formation of electronically excited lead oxide ( $PbO^*$ ) have been studied in a flow tube reactor. Only thermal excitation of Pb vapor was possible under the experimental conditions.

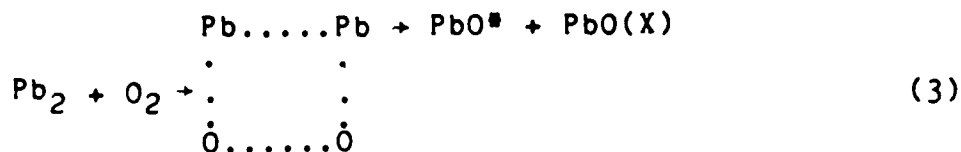
Chemiluminescence from lead oxide has been observed from the reaction between lead (Pb) vapor and  $^1\Delta O_2$ . The spectrum obtained from this emission has been compared to that obtained from the chemiluminescence observed during the reaction between Pb and ground state  $O_2$  ( $^3\Sigma$ ). Similarities and differences are discussed. A simple kinetic analysis was performed for the two reactions in which a plot of the logarithm of the intensity of a spectral band vs  $1/T \cdot K$  was prepared. From the slope of the straight lines produced, the activation energies of the two reactions were calculated. The activation energy for the  $Pb+O_2(^1\Delta)$  reaction was found to range from 12.3 to 32.4 Kcal/mole with a strong inverse dependency on oven temperature. The activation energy for the  $Pb+O_2(^3\Sigma)$  reaction was determined to

have a strong oxidizer pressure dependency. The activation energies ranged from 63.9 Kcal/mole at low oxidizer pressures to 115.3 Kcal/mole at high oxidizer pressure.

Based on this evidence from activation energies ( $E_a$ ) two different mechanisms were postulated for the reaction between Pb and  $O_2$  ( $^3\Sigma$ ) for different reaction conditions. The first is



Experimentally  $E_a = 115.3$  Kcal/mole under these conditions. Under higher pressure conditions a four-center mechanism was postulated to account for the experimental  $E_a = 63.9$  Kcal/mole.



The comparatively low activation energy for the reaction between Pb and  $^1\Delta O_2$  strongly supports the mechanism postulated by Bachar and Roserwaks<sup>(1)</sup> in which the rate controlling step was postulated to be:  $Pb(^3P_2) + O_2(^1\Delta) \rightarrow PbO(X,v) + O(^3P)$ . This reaction is expected to have a much lower  $E_a$  than those for reaction (1) or (3).

The details of the mechanisms will be discussed.

# Electronic Quenching of IF ( $B^3\Pi(0^+)$ ) by $I_2$ \*

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Interest in the quenching of the B-state of IF has been spurred by the observation of laser action originating from this state<sup>1</sup> and the relatively slow rate of electronic quenching compared to vibrational relaxation observed in collisions of IF(B) with rare gases.<sup>2</sup> The electronic quenching of IF ( $B^3\Pi(0^+)$ )  $v' = 3-6$  by  $I_2$  was studied in this work at 297 K by monitoring the time-resolved laser-induced fluorescence from IF. The rate constants for quenching of these levels are 1.5 times the gas kinetic rate constant. For  $v' = 3, 4, 5$ , and 6, we have found  $k_q = (3.6 \pm 0.1), (3.3 \pm 0.2), (3.6 \pm 0.1)$ , and  $(3.5 \pm 0.1) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively.

Fluorescence emitted when the  $v' = 3$  bandhead at 496 nm was pumped was spectrally resolved. The emission predominantly originated from the  $v' = 3$  level and terminated on a progression of levels in the ground state of IF. Less than 5% of the emission originated from  $v' = 2$ . The dispersed emission studies showed that the rate of electronic relaxation of IF by  $I_2$  greatly exceeds the vibrational relaxation rate. Furthermore, the absence of emission by  $I_2(A)$  or  $I_2(X)$  and by  $I(^2P_{1/2})$  argues against a resonant intermolecular process being the cause for the large observed rate constant and suggests that an efficient electronic to vibrational energy transfer process from IF(B) to IF(X) is responsible.

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\*This work was supported by AFWL Contract No. F29601-83-C-0049.

## PRODUCTION OF ELECTRONICALLY EXCITED STATES BY HETEROGENEOUS CATALYSIS

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The catalytic formation of electronically excited molecules by recombination of atoms with molecules or other atoms on solid surfaces has been further studied. Using nitrogen atoms mixed with discharged oxygen, the emission of the first positive system of nitrogen was readily observed as a red glow over nickel or cobalt. Using oxygen atoms, the heterogeneous formation of the  $O_2(A^3\Sigma_u^+)$  state was readily observed via the characteristic bluish -UV Herzberg emission. Addition of NO to an oxygen atom stream significantly reduced the Herzberg emission and an orange emission from  $NO_2$  was observed.

These type emissions were also studied using N-atoms and O-atoms mixed in a gas stream free of molecular oxygen. Nitric oxide was added to the N-atom stream and the rapid reaction between NO and N-atoms produced O-atoms. Using a small amount of NO, a mixture of the N and O-atoms resulted, which produced a whitish emission largely due to the beta bands of NO and some red emission of the first positive system of nitrogen. With excess NO, all N-atoms were consumed and only the O-atoms were present, and the orange glow attributed to the electronically excited  $NO_2$  molecule was observed. These results do show that the orange glow can be produced without molecular oxygen being present. It has been suggested that the orange glow observed as a result of gaseous reactions requires molecular oxygen. The results reported here suggest that the orange glow can also be generated directly in a heterogeneous catalytic process.

**BiF(AO<sup>+</sup>, v') Radiative Lifetimes, Rates for V  $\leftrightarrow$  T  
Transfer and Electronic Quenching\***

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Bismuth monofluoride (BiF) has attracted interest as a potential lasing species (BiF(A $\rightarrow$ X)) in a chemically pumped visible laser system. Here we report measurements of the BiF(AO<sup>+</sup>, v'=0,1,2,...) radiative lifetimes, rates for V  $\leftrightarrow$  T transfer and electronic quenching by Ar using time resolved laser induced fluorescence (LIF). The radiative lifetimes are greater than 1 s for v' < 11. Using a numerical model to fit the experimental data, we are able to estimate the rates for electronic quenching and intervibrational (V  $\leftrightarrow$  T) relaxation of BiF(A, v').

For the quenching studies BiF is produced by injecting a F<sub>2</sub>/He mixture into a Bi/Ar flow from a Broida-type oven. The radiative lifetime measurements are taken at low pressure to minimize collisional quenching and radiation imprisonment. Specific vibrational bands in BiF(A $\rightarrow$ X) are excited using an excimer pumped dye laser with (0.1 cm<sup>-1</sup> bandwidth). The LIF emission is collected by a PMT (EMI 6256S/S-20) through filters (1.0 nm FWHM) which effectively isolate individual (v', v'') bands. Verification experiments were performed using a monochromator at greatly reduced signal levels. Experiments included monitoring the emission from both the pumped v' state and from adjacent vibrational levels. The PMT signal is digitized using a 100 MHz transient recorder and averaged by a computer. Experiments are conducted at 10 Hz.

Stern-Volmer plots give total removal rates of the pumped level which increase with v' in the range 5 x 10<sup>-13</sup> to 3 x 10<sup>-12</sup> cm<sup>3</sup> molec<sup>-1</sup>sec<sup>-1</sup>. From the computer modeling studies, we estimate the rates for BiF(A, v'=0  $\rightarrow$  1) vibrational redistribution and BiF(A, v'=0) electronic quenching by Ar to be k<sub>v</sub> ~ 4 x 10<sup>-11</sup> cm<sup>3</sup> molec<sup>-1</sup>sec<sup>-1</sup> and k<sub>q</sub> ~ 4 x 10<sup>-13</sup> cm<sup>3</sup> molec<sup>-1</sup>sec<sup>-1</sup> respectively. Work is currently underway to expand the quenching studies to include He and SF<sub>6</sub> and to refine our kinetic modeling.

\* This work was conducted under U. S. Air Force Space Division (AFSD) Contract FO 4701-84-C-0085.

Electronic-to-Vibrational Energy Transfer in the Deactivation  
O(<sup>1</sup>D) By CO<sub>2</sub>

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Vibrationally excited CO<sub>2</sub> (m,n,p) was prepared by collisional deactivation of O(<sup>1</sup>D), which was generated by flash photolysis of O<sub>3</sub>/N<sub>2</sub>/CO<sub>2</sub> mixtures with a KrF laser. It appears that vibrationally excited nitrogen is intermediate in the electronic-to-vibrational energy conversion. The initially generated excited states of CO<sub>2</sub> are above the (001) level, but redistribution via a rapid cascade occurs. The system dynamics was followed by recording the time dependent fluorescence at the 4.3 μm band. Appropriate use of CO<sub>2</sub> cold-gas-filters permitted partial resolution of the emission which arose from (001), (011) and higher lying states. Quantitative results and a discussion of the CO<sub>2</sub> (m,n,p) relaxation kinetics will be presented.

## Resonance Optoacoustic Detection of NO by Double Modulation.

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The resonant optoacoustic effect and a double modulation technique are exploited to create a sensitive detection scheme for trace concentrations of NO in the presence of interfering species. Resonance optoacoustic detection takes advantage of energy transfer to form standing pressure waves in a relatively large (200 cm<sup>3</sup>) cell. These standing waves provide signal gain factors approaching 1000. The double modulation technique combines Zeeman tuning of NO with mechanical chopping of a stabilized line-tuneable CO laser. Zeeman shifting NO ro-vibrational transitions into and out of resonance with the CO laser produces a derivative signal at  $\omega_1$  unique to the NO molecule due to its Zeeman tuning rate. The laser is mechanically chopped at  $\omega_2$  and the detection locked to  $\omega_1 \pm \omega_2$ . In this scheme inphase noise signals at either  $\omega_1$  or  $\omega_2$  are not seen by the detector. Energy transfer rates for collisional relaxation of NO, v=1 by added buffer gas determines the minimum total pressure at which one can operate. Loss mechanisms related to the choice of buffer gas and cell dimensions limit the signal levels available for detection.

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VIBRATIONALLY EXCITED POPULATIONS FROM I.R. MULTIPHOTON ABSORPTION:  
OPTOACOUSTIC AND REACTION YIELD MEASUREMENTS

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(Work done at SRI, Menlo Park, CA)

VIBRATIONALLY EXCITED POPULATIONS FROM I.R. MULTIPHOTON ABSORPTION:  
INFRARED FLUORESCENCE MEASUREMENTS

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**FIRST OBSERVATION OF THE RESOLVED SPECTRUM OF THE  
FORMALDEHYDE ( $T_1 - S_0$ ) TRANSITION FROM THE CHEMILUMINESCENT  
SELF-REACTION OF METHOXY RADICALS**

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Reaction of ground state F atoms with methanol, highly diluted in helium, in a fast flow reactor at 2 Torr and 298 K results in chemiluminescence (CL) which is faintly visible in a dark room. When  $O_2$  was rigorously excluded from the reactant gases, the CL spectrum consisted of high vibrational overtones of HF, formaldehyde ( $S_1 - S_0$ ) and a previously unobserved band system which we postulated to be formaldehyde ( $T_1 - S_0$ ). The  $T_1$  and  $S_0$  states have similar geometries and the vibronic selection rules are the same for both of their transitions to the ground state. Thus we constructed a template for  $T_1 - S_0$  based upon Brand's assignment of the  $S_1 - S_0$  transition, and this matched the band positions of our observed spectrum. The intensity of the  $T_1$  emission was correlated with the relative concentration of methoxy, measured by laser induced fluorescence. We attribute both  $T_1$  and  $S_1$  state formation to the self-reaction of methoxy radicals. Addition of  $O_2$  selectively quenched the  $T_1$  state. Under our best  $O_2$  free conditions  $T_1:S_1 = 2000$  and the quantum yield for  $T_1$  was on the order 0.001. Addition of biacetyl, which has a lower  $T_1$  energy than formaldehyde, resulted in the replacement of formaldehyde ( $T_1 - S_0$ ) by the well known biacetyl ( $T_1 - S_0$ ) spectrum.

# KINETIC STUDIES OF $\text{OH}(\text{A}^2\Sigma^+)$ PRODUCED BY KrF LASER MULTIPHOTON EXCITATION OF $\text{H}_2\text{O}$

by

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Electronic relaxation rates of  $\text{OH}(\text{A}^2\Sigma^+)$  with various atmospheric gases are necessary parameters in laser-induced fluorescence diagnostics of ground state  $\text{OH}(\text{X}^2\Pi)$ , important in atmospheric and combustion chemistry<sup>1-2</sup>. The rotational level dependence of electronic quenching of  $\text{OH}(\text{A}^2\Sigma^+, v'=0)$  may also provide an understanding into the bimolecular energy transfer mechanism from electronically excited diatomic molecules<sup>3-5</sup>.

In the present work the rotational state-specific rate constants of  $\text{OH}(\text{A}^2\Sigma^+, v'=0)$  quenching by  $\text{H}_2\text{O}$ , CO and  $\text{N}_2$  over the range of rotational levels  $N'=13-17$  have been obtained. The hydroxyl radicals were formed in a wide range of rotational levels (up to  $N'=20$ ), following the coherent two-photon excitation and fragmentation of  $\text{H}_2\text{O}$  by a KrF laser at 248nm<sup>6</sup>. Their time-resolved photofragment fluorescence was monitored for specific rotational levels by adequately resolving it.

The results indicate that the dependence of quenching rates on  $N'$  is different for various collisional partners, which can imply that several deactivation channels may compete.

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Time-Resolved Optoacoustic Measurements of  
Vibrational Relaxation of Highly Excited Molecules\*

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A new form of time-resolved optoacoustics has been developed. In this method a fast piezoelectric transducer placed within a large chamber is used to detect individual compression and rarefaction waves generated by the relaxing gas. This technique has a large dynamic range and is capable of measuring the microcanonical VT relaxation rates of molecules prepared in various initial energy states. We have applied this method to the relaxation of  $\text{SF}_6$  in Ar, and have determined the relaxation rate of  $\text{SF}_6$  for initial excitation energies ranging from  $1000 \text{ cm}^{-1}$  all the way up to dissociation.

\*Support by the NSF is gratefully acknowledged.

POSTER SESSION D

Kinetics of One-Electron Transfer Reactions Involving  
 $\text{ClO}_2$  and  $\text{NO}_2$  in Aqueous Solutions

by

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Chlorine dioxide and nitrogen dioxide are simple inorganic free radicals which undergo one-electron reduction to chlorite and nitrite anions, respectively. These reactions are important for practical reasons ( $\text{ClO}_2$  is a bleaching and disinfecting agent;  $\text{NO}_2$  is a reactive air pollutant) and because the reactions of these simple radicals may be subject to theoretic treatment.

Using pulse radiolysis for the generation of free radicals and kinetic absorption spectroscopy to monitor them, we have measured rate constants for several reactions of  $\text{ClO}_2$  and  $\text{NO}_2$  with organic and inorganic species and for the reactions of several organic and inorganic free radicals with  $\text{ClO}_2^-$  and  $\text{NO}_2^-$ , producing  $\text{ClO}_2$  and  $\text{NO}_2$ . In addition, equilibrium constants were determined for the reactions of  $\text{ClO}_2$  with aniline and N, N-dimethylaniline. Since the  $\text{ClO}_2/\text{ClO}_2^-$  redox potential is well known (0.936V), this has allowed us to derive one-electron redox potentials for these aromatic amines.

The kinetics of the reactions of  $\text{ClO}_2$  and  $\text{NO}_2$  have rate constants which are consistent with simple electron-transfer theory. The notable exception is the reaction of  $\text{NO}_2$  with  $\text{SO}_3^{2-}$ , which suggests that this reaction is an oxygen atom transfer, not electron transfer, reaction.

# Polymerization of $\text{NO}_2$ and $\text{NO}$ in a Supersonic Nozzle Expansion

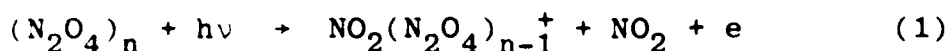
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$\text{NO}_2$ ,  $\text{NO}$  and  $\text{NO}_2$ - $\text{NO}$  binary clusters were produced in a supersonic nozzle beam and detected by a photoionization mass spectrometry. In the case of the  $\text{NO}_2$  cluster, odd number cluster ions such as  $(\text{NO}_2)_{2n+1}^+$  are dominant than  $(\text{NO}_2)_{2n}^+$  ions when an Ar lamp having a LiF window was used as a photoionization light source. The result was explained as follows; 1)  $\text{N}_2\text{O}_4$  molecules are produced. 2)  $\text{N}_2\text{O}_4$  molecules polymerize and  $(\text{N}_2\text{O}_4)_n$  clusters are produced. Then neutral clusters formed are the even number cluster of  $\text{NO}_2$ . 3) When the  $(\text{N}_2\text{O}_4)_n$  molecule is photoionized, the  $\text{NO}_2(\text{N}_2\text{O}_4)_{n-1}^+$  is produced.



And finally the odd number cluster ions of  $\text{NO}_2$  were observed.

When  $\text{NO}$  gas from Matheson was expanded, signals of  $(\text{NO})_2^+$ ,  $\text{N}_2\text{O}_3^+$ ,  $(\text{NO})(\text{N}_2\text{O}_3)_{1\sim 4}^+$ , and  $(\text{NO}_2)(\text{N}_2\text{O}_3)^+$  were observed. Among above ions,  $\text{N}_2\text{O}_3^+$ ,  $(\text{NO})(\text{N}_2\text{O}_3)_{1\sim 4}^+$  and  $(\text{NO}_2)(\text{N}_2\text{O}_3)^+$  ion signals disappeared when  $\text{NO}$  (Matheson) gas was purified by passing through a column of Ascarite. Then only the  $\text{NO}$ -dimer was detected from the pure  $\text{NO}$  gas. In the case of the  $\text{NO}$ - $\text{NO}_2$  binary clusters, ion signals of  $(\text{NO})_2^+$ ,  $\text{N}_2\text{O}_3^+$ , and  $(\text{NO}_2)(\text{N}_2\text{O}_3)_n^+$  were observed. Above ions were detected by both Ar and Kr lamps. Changes of the signal intensities by the stagnation pressure and the mixing ratio of  $\text{NO}$  and  $\text{NO}_2$  will be discussed.



# MICROWAVE ABSORPTION TECHNIQUE FOR STUDYING

## SECONDARY ELECTRON PROCESSES

by

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The attenuation of microwave power when propagating through a dielectric medium is proportional to the sum of the products of concentration and mobilities of all charged species present in the medium. As mobilities of electrons are very much larger than other species this effect can be used to study processes involving electrons produced during the pulse-radiolysis of gases and gas mixtures.

Thermal electron attachment to halocarbons has become of interest in investigations of the chemistry of the upper atmosphere and the study of charge transfer reactions in general. In this study, using circuitry designed to measure the microwave attenuation and a Febetron 706 electron pulser as a means of providing the initial electron concentration, thermal electron attachment rate constant of well-known electron capture agents and a number of halocarbons have been measured.

Compounds	$k(\text{dm}^3 \text{ mole}^{-1} \text{ s}^{-1})$
$\text{SF}_6$	$1.24 \times 10^{14}$
$n\text{-C}_4\text{F}_{10}$	$1.69 \times 10^{10}$
$\text{CF}_3\text{Cl}$	$8.3 \times 10^7$
$\text{CF}_3\text{Br}$	$2.26 \times 10^{12}$
$\text{CF}_3\text{I}$	$1.16 \times 10^{14}$

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Kinetics and Mechanism of Hexacyanoferrate (III) Oxidation  
of Arylthioacetic Acids

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The kinetics of oxidation of phenylthioacetic acid and several substituted phenylthioacetic acids with hexacyanoferrate (III) have been investigated in alkaline medium. The reaction is found to be first order each in the oxidant, substrate and  $\text{OH}^-$ . The involvement of an equilibrium between ferricyanide and ferrocyanide has been inferred from the decrease of rate with an increase of [ferrocyanide]. The study of substituent effect establishes that electron withdrawing groups accelerate while electron releasing groups (with the exception of methoxyphenylthioacetic acids) retard the rate of oxidation. An excellent Hammett correlation is obtained with nine arylthioacetic acids ( $\rho = +1.22$ ). The substituents  $\text{p-OCH}_3$ ,  $\text{m-OCH}_3$  and  $\text{p-NO}_2$  accelerate the rate more than anticipated and this interesting behavior may possibly be due to the stabilization of the radical intermediate by resonance through sulphur atom.

Kinetics of hexacyanoferrate (III) oxidation of phenylacetic acid and phenylsulphonylacetic acid show that the order of reactivity is phenylacetic acid  $\ll$  phenylsulphonylacetic acid  $<$  phenylsulphonylacetic acid. The absence of any reaction with phenoxyacetic acid reveals the involvement of d-orbital of sulfur in the oxidation of phenylthioacetic acid. With phenylthioacetic acid as the substrate, the product is identified to be  $\alpha$ -hydroxyphenylthioacetic acid. A suitable mechanism has been proposed based on the kinetic results.

Reactivity and Percentage Deamination in the Pulse  
Radiolysis of N-Alkyl Substituted Arylalkylamines

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Abstract

To correlate our earlier results of effects of substituents in the alkyl chain of benzylamine in the pulse radiolysis experiments with the N-alkyl substituted derivatives, the  $e_{aq}^-$  reactions of N-methylbenzylamine and N, N-dimethylbenzylamine were studied. The +I effect of the alkyl groups replacing the H atoms of an amine nitrogen was expected to increase the electron density on the nitrogen atom. The percentage deamination in the case of N-methylbenzylamine was observed to be  $42 \pm 5\%$ , which was the same as that of benzylamine and was less compared to that of benzylamine ( $70 \pm 5\%$ ). However, the reactivity of the N-methylbenzylamine towards  $e_{aq}^-$  was not decreased much. In the case of N, N-dimethylbenzylamine, its reactivity towards  $e_{aq}^-$  was increased to  $2.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ , contrary to what was expected from the +I effect of the methyl group. This might reflect the strain introduced into the molecule by the introduction of two bulky methyl groups around the nitrogen atom. This effect could be correlated with the peculiar order of base strength in these amines (pKa of benzylamine = 9.35, N-methylbenzylamine = 9.58 and N, N-dimethylbenzylamine = 9).

\*Work done at the Radiation Laboratory, University of Notre Dame, USA

# HYDROGEN ABSTRACTION RATES BY RESONANCE STABILIZED RADICALS IN THE LIQUID PHASE

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Absolute rate constants for hydrogen abstraction by diphenylmethyl and fluorenyl radicals from several donors were measured in the liquid phase at 275°C. Values are found to be comparable to those for alkyl radical hydrogen transfer reactions having similar overall thermochemistry. For one reaction pair, tetralin-diphenylmethyl radical, the rate constant was measured over a temperature range of 225-300°C. The least-squares-derived Arrhenius expression for this reaction is  $10^{10.1} \exp(10300/T) \text{M}^{-1} \text{s}^{-1}$ . The pre-exponential factor seen here is higher than those commonly observed for hydrogen transfer reactions in gas phase systems. Our results for these reactions are compared to those from another studies involving hydrogen transfer to benzyl radicals.<sup>2,3</sup> In addition, by measuring forward and reverse rates, a value of 10 was determined for the equilibrium constant of the reaction, diphenylmethyl + fluorene = diphenylmethane + fluorenyl at 275°C. This indicates a higher relative stability for the fluorenyl radical and/or different entropy effects in the forward and reverse reactions.

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Work supported by the Gas Research Institute.

## BENZENE HYDROGENATION KINETICS: A TRANSIENT APPROACH.

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Although widely used and studied as a model reaction in heterogeneous catalysis, the hydrogenation of benzene still gives rise to much controversy, particularly upon basic assumptions as the competitive or non competitive adsorption of benzene and hydrogen onto the catalytic surface. This led logically to highly diverging kinetic models. In this respect, a precise knowledge of the catalyst adlayer composition in the reaction course would greatly strengthen any kinetic modelisation of the reaction.

In the present paper, we report the way to determine the amounts of reactive adspecies in the steady-state regime of benzene hydrogenation on a series of supported or unsupported transition metal catalysts. The method of isotopic transients which has been recently described for the case of methanation and Fischer-Tropsch synthesis has been adapted for the present hydrogenation process. The basic principle consists of replacing abruptly one of the feed components - e.g. benzene - by its labelled equivalent - e.g. deuterated benzene - and to follow by on-line mass spectrometry the transient decay of the unlabelled product - light cyclohexane - and the simultaneous breakthrough of the labelled species. This procedure is assumed to let the steady-state surface equilibrium unperturbed (to the extent that the changes in reactivity due to the isotopic composition of the reacting species are limited). The concentration of the reactive adspecies are estimated from the delays observed between reactant and product transient curves (corrected from chromatographic side-phenomena) and from the steady-state intrinsic rate of hydrogenation.

In apparent contrast with the observed orders versus hydrogen and benzene pressure, the concentration of activated benzene is shown to be very low and the metallic surface mainly covered with hydrogen. The changes in surface composition according temperature and reactant pressure are studied. A scheme of competitive adsorption between hydrogen and benzene onto the metallic surface, including the size requirements for the benzene activation sites, is proposed, which provides a firm basis for further mechanistic investigations.

## ISOTOPE EXCHANGE VIA IONIC REACTIONS

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Isotope exchange can occur via either ionic reactions or neutral reactions. The behavior of the two is strikingly different and illustrates fundamental differences between ionic reactions and neutral reactions.

Examples of ionic isotope-exchange reactions are:  $^{18}\text{OH}^- + \text{H}_2\text{O} = \text{H}_2^{18}\text{O} + \text{OH}^-$  and  $\text{HCO}^+ + \text{D} = \text{DCO}^+ + \text{H}$ . They typically exhibit the following features: (1) The rate constants show anti-Arrhenius behavior, increasing with decreasing temperature to achieve maximum values in the limit of absolute zero. (2) This behavior may be described in terms of motion over hypersurfaces, which are concave rather than convex, and where the motion involves passage through basins rather than over barriers. (3) Because motion does not require the surmounting of barriers, no evidence is shown for tunnelling at any temperature.

Ionic isotope-exchange reactions occur under either thermodynamic control or kinetic control. These may be distinguished using rate measurements together with thermodynamic or statistical thermodynamic analysis. For thermodynamic control, atomic motion within the reaction intermediate must occur on a time scale short compared to the intermediate lifetime: an example is  $\text{OH}^- + \text{D}_2\text{O}$  at 300K. For kinetic control, the time scale of the atomic motion is comparable to the lifetime or slower: an example is  $\text{CH}_5^+ + \text{CD}_4$  at 300K. The driving force is the free energy decrease; in the high temperature limit, this becomes entropic, leading to statistical product distributions; in the low temperature limit, this becomes enthalpic and zero-point energy differences determine the product distribution.

Further conditions follow from the identity of the reactants - whether they are closed-shell/closed-shell, closed-shell/open-shell or open-shell/open-shell. For closed-shell/closed-shell reactants, the minimum energy pathway for hydrogen isotope exchange is shown to involve proton transfer within the intermediate, and simple rules are formulated to show if it is allowed or forbidden. For the other two categories, each system is a particular case, not susceptible to generalization.

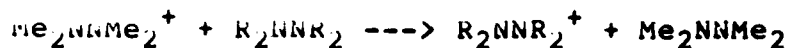
Applications include: (1) The jump time of the proton from one water molecule to another water molecule within the intermediate  $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O} = \text{H}_2\text{O} \cdot \text{H}_3\text{O}^+$  is shown to be less than 25 ps at 500K. (2) The zero-point energy of  $\text{CH}_5^+$  is shown to be  $31 \pm 1$  kcal/mol. (3) Structural isomers, such as  $\text{HCO}^+$  and  $\text{COH}^+$ , may be identified kinetically and thus isomerization may be monitored. (4) Pathways may be identified whereby interstellar molecules become enriched in deuterium.

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### SLOW ORGANIC ELECTRON TRANSFER REACTIONS

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Most exoergic gas-phase electron transfer reactions proceed near unit collision efficiency. In contrast, electron transfer reactions between hydrazines, e. g., reaction 1, are slow, with collision efficiencies of  $10^{-2}$  to  $10^{-5}$ .



The rate constants show small positive temperature coefficients, with Arrhenius activation energies of -2 to 3 kcal/mol.

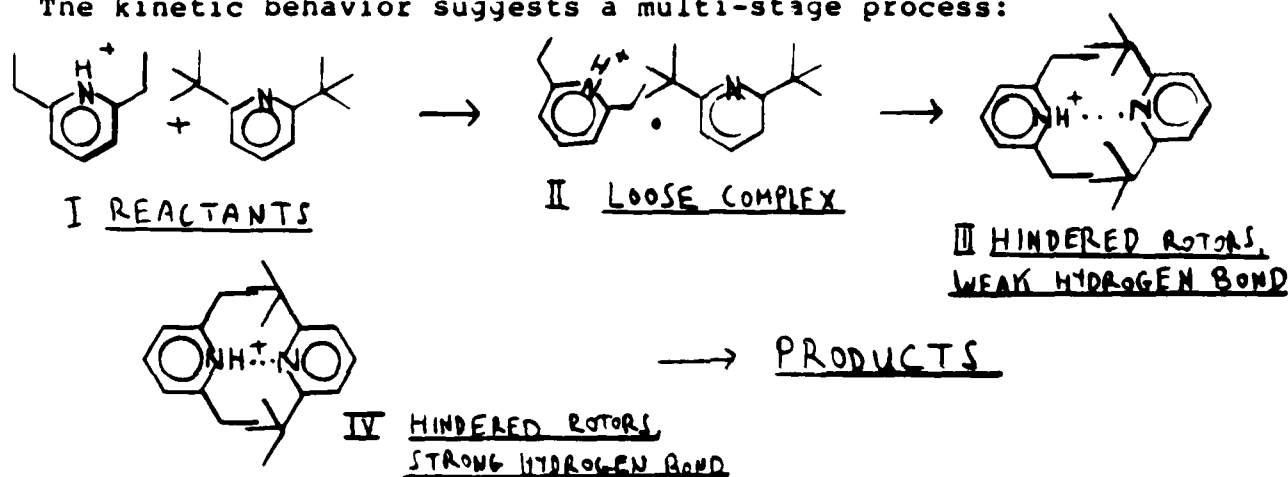
The ionization of hydrazines involves a geometry change from a perpendicular  $\text{R}_2\text{N} - \text{NR}_2$  to a planar  $\text{R}_2\text{N} - \text{NR}_2^+$  with a three-electron N - N bond. The slow rates of electron transfer may be therefore attributed to an energy barrier in a transition state where both the electron donor and acceptor are strongly distorted from the ground-state geometry. Using the temperature coefficients and the measured bonding energy of the intermediate complex, the internal barrier is estimated as about 15 kcal/mol, about one-third of the barrier for vertical transfer (in the Franck-Condon sense). Further observations show that low efficiencies require geometry distortion of both reactants. This is indicated by the observation that when only the electron donor is an alkylhydrazine, while the acceptor is a rigid ion, the reaction efficiencies increase by factors of 10 - 1000.

Free Energy Surfaces with Multiple Wells. Slow Proton Transfer Reactions and Entropy Barriers Due to Steric Hindrance.

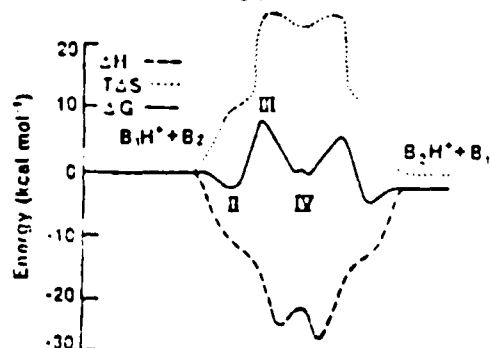
Michael Meot-Ner (Mautner), Chemical Kinetics Division, National Bureau of Standards, Gaithersburg, MD 20899

Unlike most exothermic proton transfer reactions, proton transfer from 2-alkyl and 2,6-dialkyl pyridines to 2,6-di-*t*-butyl pyridine is slow. The reaction efficiencies at 470 K decrease from unity when the reactant ion is slightly hindered (2-Me-PyrH<sup>+</sup>), to 10<sup>-2</sup> with a moderately hindered reactant (2,6-di-EtPyrH<sup>+</sup>) and 10<sup>-4</sup> with the strongly hindered 2,2-di-*i*PrPyrH<sup>+</sup>. The rate constants exhibit very large negative temperature coefficients, up to  $k T^{-10}$  (equivalent to a negative activation energies up to -14.5 kcal/mol).

The kinetic behavior suggests a multi-stage process:



In the first stage the reagents form a loosely bonded electrostatic complex II. Steric hindrance results in a free energy barrier III before the transition to the hydrogen-bonded complex IV. This barrier arises when the rotors are hindered (large negative  $S$  term), but the incipient hydrogen bond is too extended to compensate (small negative  $H$  term). The enthalpy, entropy and free energy surfaces may be drawn as follows:



Back-dissociation from the loose complex II to reactants increases with temperature, which accounts for the negative temperature coefficients of the overall forward reactions.



# The Proton in Multisolvant Clusters: The Acetonitrile-Water System

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Two cationic species present in the stratosphere are  $(\text{H}_2\text{O})_n\text{H}^+$  and  $(\text{H}_2\text{O})_n\text{X}^+$ , where  $X = 41$  amu. The most viable candidate for  $X$  to date is  $\text{CH}_3\text{CN}$ . Part of the evidence in support of  $\text{CH}_3\text{CN}$  as  $X$  is from the selected ion flow tube (SIFT) study of the reactions of  $\text{CH}_3\text{CN}$  with  $(\text{H}_2\text{O})_n\text{H}^+$  conducted by Smith et al. [Smith, D.; Adams, N.G.; Alge, E.; *Planet. Space Sci.* 1981, **29**, 449]. They found that  $\text{CH}_3\text{CN}$  rapidly replaces  $\text{H}_2\text{O}$  in these ions, with the exception of the last  $\text{H}_2\text{O}$  in  $(\text{H}_2\text{O})(\text{CH}_3\text{CN})_2\text{H}^+$  and  $(\text{H}_2\text{O})(\text{CH}_3\text{CN})_3\text{H}^+$ . We have examined the thermochemistry of these reactions via both pulsed high pressure mass spectrometric and ab initio techniques. The objectives of this work were to determine: 1) the optimum structures and experimental and theoretical dissociation energies of  $(\text{H}_2\text{O})_n(\text{CH}_3\text{CN})_m\text{H}^+$ ,  $n = 1-4$ ,  $m = 1-3$ ; 2) the amount of charge transfer through the hydrogen bonds and the structural reorganization around the proton produced by addition of solvent molecules; 3) the relationship between structure, charge transfer, and energetics; 4) why the last  $\text{H}_2\text{O}$  molecule is not readily replaced in the  $(\text{H}_2\text{O})(\text{CH}_3\text{CN})_m\text{H}^+$ ,  $m = 2,3$ , cations.

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# HOW DOES SOLVATION AFFECT REACTIVITY?

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It is now possible to produce in the gas phase selectively solvated ions holding one, two, or three solvent molecules and to study their reactions over an extended temperature range. The following questions can thus be asked: How is reactivity affected by the selective solvation of the reactants? How is this changed by temperature? Does it change if the identity of the solvent molecule is changed? Is the behavior different for different types of reaction?

Rate constants have been measured on the AFGL Selected Ion Flow Tube over the temperature range 200 - 500K for the reactions of the selectively solvated ions  $\text{OH}^-(\text{H}_2\text{O})_{0,1,2,3}$  with hydrogen halides and methyl halides. A similar study has been made for the ionic reactants  $\text{CH}_3\text{O}^-(\text{CH}_3\text{OH})_{0,1}$ .

Different behavior is found for different types of reaction, specifically, proton transfer and nucleophilic displacement. Proton transfer always occurs on every collision, provided that it is energetically possible; this holds at all temperatures and whatever the extent of solvation; and solvate is transferred readily from reactant ion to product ion to drive the proton transfer where the energetics demand it. Nucleophilic displacement, on the other hand, shows a negative temperature dependence that is accentuated with increasing solvation; solvate is not transferred readily from reactant ion to product ion; and reaction is quenched for the addition of only a few solvate molecules.

Such studies raise general questions. Given the utility of Arrhenius plots, what can be learned from Arrhenius plots as a function of solvation number? What bearing have these for reaction in solution? The case is made that such gas phase studies explore the participation of solvate in the absence of bulk solvent.

The comparison between gas phase and solution is invariably instructive. The species  $\text{PO}_3^-$  is a case in point. Identified by biochemists to be a highly reactive intermediate in phosphorylation and phosphate ester hydrolysis,  $\text{PO}_3^-$  is shown in the gas phase to be thermodynamically stable and chemically inert. The question thus arises as to how hydration can make a stable species unstable and an unreactive species reactive.

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<sup>2</sup> AFSC-URRP Visiting Professor, 1984-1985. Permanent address: Department of Chemistry, Brandeis University, Waltham, MA 02254

Thermochemistry of Solvation of  $\text{NO}_2^-$  and  $\text{C}_6\text{H}_5\text{NO}_2^-$  by  
Polar Molecules in the Vapor Phase.  
Comparison with  $\text{Cl}^-$ , and Variation with Ligand Structure.

by  
L. Wayne Sieck

ABSTRACT

The stabilities of  $\text{NO}_2^- \cdot \text{X}$  and  $\text{C}_6\text{H}_5\text{NO}_2^- \cdot \text{X}$  association ions, where X is a dipolar protic or aprotic organic solvent, have been investigated by the technique of pulsed high-pressure mass spectrometry. For comparison, analogous measurements were made with  $\text{Cl}^-$  for certain model ligands (X). Equilibrium constants were determined as a function of temperature in order to define  $\Delta H$  and  $\Delta S$  values for solvation. The solvation energies vary as  $\text{NO}_2^- > \text{Cl}^- > \text{C}_6\text{H}_5\text{NO}_2^-$  for liquids having -OH sites (alcohols, carboxylic acids). Association entropies are constant at  $-26 \pm 1$  for cluster ions incorporating  $\text{NO}_2^-$  or  $\text{C}_6\text{H}_5\text{NO}_2^-$  and protic ligands, but vary significantly when  $\text{Cl}^-$  is the core ion. For aprotic ligands, such as  $\text{X} = \text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{NO}_2$ ,  $(\text{CH}_3)_2\text{CO}$ , and  $(\text{CH}_3)_2\text{SO}$ , the values of  $\Delta H$  and  $\Delta S$  for both  $\text{NO}_2^- \cdot \text{X}$  and  $\text{C}_6\text{H}_5\text{NO}_2^- \cdot \text{X}$  also exhibit large variations. In this case the differences are interpreted in terms of the blocking or partial blocking effects of the methyl groups, which shield the group having most of the dipole moment of the ligand ( $-\text{C} \equiv \text{N}$ ,  $-\text{S}=\text{O}$ , etc.). Probable structures for some of the association ions are presented and discussed.

Reaction Kinetics for Aerosol Formation in  
 $O_3-C_2H_4$  and  $O_3-C_2H_4-SO_2$

E. R. Manzanares, Masako Suto and L. C. Lee  
 Department of Electrical and Computer Engineering  
 San Diego State University  
 San Diego, California 92182

The optical detection method is applied to investigate the kinetics of aerosol formation from the reactions of  $O_3-C_2H_4$  and  $O_3-C_2H_4-SO_2$  in a flow tube. The aerosol concentrations were measured by the aerosol light scattering intensity (ALS). The chemiluminescence intensity (CL) from the reactions were also monitored.

The ALS in  $O_3-C_2H_4$  is proportional to  $[O_3]^{2.5} [C_2H_4]^{1.8}$ . Addition of  $H_2O$  increases the ALS without affecting the CL,  $NO_2$  reduces both ALS and CL, while  $H_2$ ,  $CO_2$ ,  $N_2$ , propane and methane affects neither ALS or CL. The conversion of H to  $HO_2$  and the subsequent secondary reactions involving  $HO_2$  are important in the formation of aerosols.

Addition of  $SO_2$  to  $O_3-C_2H_4$  increases aerosol formation without affecting the chemiluminescence. At a fixed  $[C_2H_4]$ , the ALS is proportional to  $[O_3]$ . This supports the mechanism that the sulfur-containing aerosol ( $H_2SO_4$ ) is formed from the oxidation of  $SO_2$  by an intermediate product ( $CH_2O_2$ ) of the primary reaction,  $O_3 + C_2H_4$ . Addition of  $H_2O$  or  $NO_2$  reduces ALS which is used to infer rate constant of its reaction with  $CH_2O_2$ . The ratio of the rate constants for the reactions of  $SO_2$  and  $H_2O$  with  $CH_2O_2$  is estimated to be  $(4.3 \pm 2) \times 10^3$ , and that of  $SO_2$  and  $NO_2$  is  $74 \pm 20$ . These reactions are important for assessing the contribution of  $O_3$ -olefin reactions in sulfuric acid formation in the atmosphere.

This work is supported by NSF under Grant No. ATM-8203948.

# Three-Body Association Rate Coefficients as a Function of Temperature and Cluster Size

A.A. Viggiano and John F. Paulson

Air Force Geophysics Laboratory

Hanscom AFB, MA 01731

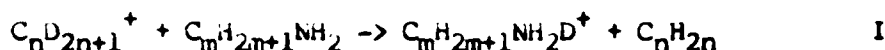
The three-body reaction rate coefficients are reported for the association of  $\text{NO}_3^-(\text{HNO}_3)_a$  and  $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_b (\text{HNO}_3)_c$  to  $\text{HCl}$  for  $a = 0, 1$  and  $2$ ;  $b = 0, 1, 2$ , and  $3$ ; and  $c = 0$  and  $1$ . The measurements were made in three buffers: hydrogen, helium, and nitrogen. The temperature dependence of these reactions was found to vary as  $T^{-n}$ . The measurements show  $n$  to increase significantly with cluster size. For  $a = 0, 1$  and  $2$  in a hydrogen buffer,  $n$  is equal to  $2.06, 4.17$  and  $5.59$ , respectively. For  $\text{HSO}_4^-$  core ions, the increase is even more dramatic. For  $b = 0$  and  $1$  ( $c = 0$ ) in a hydrogen buffer,  $n$  is equal to  $2.95$  and  $6.93$ , respectively, and  $n = 4.6$  for  $b = 0$  and  $c = 1$ . The temperature exponent for  $\text{HSO}_4^-$  core ions is greater than that for  $\text{NO}_3^-$  core ions by about  $1/2$ . The magnitudes of the rate coefficients vary in a more complicated manner, at first increasing as more ligands are added, then decreasing significantly, so that for  $b = 3$ , the rate coefficient was too small to measure. Qualitatively, the increase in  $n$  with cluster size can be explained by the low frequency vibrations of the cluster bonds.

On the Mechanism of the Reactions of Alkyl Ions with Alkylamines: Competing Proton Transfer and Condensation Reactions.

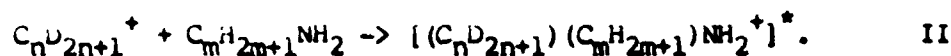
by

P. Ausloos and S. G. Lias  
Center for Chemical Physics  
National Bureau of Standards  
Gaithersburg, Maryland 20899

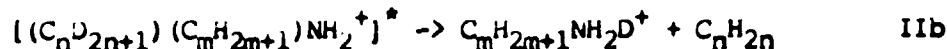
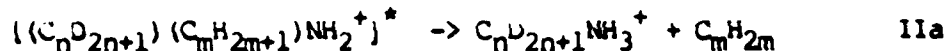
The reactions of ethyl, isopropyl, and t-butyl ions with alkylamines (ethylamine, n-propylamine, isopropylamine, t-butylamine, t-amylamine, cyclonexylamine, and di-n-propylamine) have been examined in an ion cyclotron resonance spectrometer (ICR). Use of deuterium-labelled reactant ions permitted a detailed examination of the relative probabilities of the two competing reaction channels demonstrated previously by Meot-Ner. These are deuterium/proton transfer:



and condensation:



At the low pressures of an ICR experiment ( $\sim 10^{-6}$  torr), the condensation ions all dissociate through one of two paths, IIa or IIb:



(where the second channel yields products identical to those formed in the direct deuterium/proton transfer). The results demonstrate that in most systems, dissociation of  $[(C_n D_{2n+1})(C_m H_{2m+1})NH_2]^+$  follows either channel a or b, but not both simultaneously; furthermore, (as suggested by the photodissociation results of Moylan and Brauman) the channel which is followed is not necessarily the more exothermic. The results are compatible with a mechanism in which the weakest C--N bond in the condensation ion undergoes scission to give a complex containing an alkyl ion ( $C_n D_{2n+1}^+$  or  $C_m H_{2m+1}^+$ , whichever is energetically favored) and the corresponding amine, followed by proton transfer in the complex to yield the final products. In systems for which the condensation-dissociation channel proceeds through IIa, the branching ratio IIb/I can be derived from the relative abundances of the  $C_n D_{2n+1} NH_3^+$  and  $C_m H_{2m+1} NH_2 D^+$  products. This ratio varies between 0.28 and 1.6 for reactions of the ethyl ion, 0.16 and 0.51 for the propyl ion, and is about 0.05-0.06 for those t-butyl reactions for which the ratio can be derived (in excellent agreement with the published results of Meot-Ner who observed stabilized condensation ions in a high pressure mass spectrometer for several of the same systems).

The study of these systems is complicated by the occurrence of secondary reactions, and, in some cases, by the presence of impurities commonly found in commercial amine samples. The use of deuterium labelling and carefully chosen experimental conditions to circumvent the difficulties will be described.

## PICOSECOND AND NANOSECOND LASER PHOTOLYSES OF DINITROTOLUENES IN SOLUTION.

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Naval Research Laboratory, Washington, D. C. 20375; \*Georgetown University,  
Washington, D. C. 20057; #Center for Fast Kinetics Research, University of  
Texas, Austin, TX 78712.

We have measured time-dependent absorption spectra following 266 nm picosecond (30 ps, ca. 2-3 mJ) and nanosecond (12 ns, ca. 8 mJ) laser photolyses of 2,4-dinitrotoluene and 2,6-dinitrotoluene in several solvents. In aqueous acidic media, we believe that intramolecular hydrogen transfer occurs in the lowest triplet states to yield the aci-quinoid isomers. The long term products in aqueous basic media are the dinitrobenzyl anions which are identified by their characteristic absorption spectra. The similarity of the transient spectra in acidic media and those obtained in nonpolar media suggests that the aci-form predominates in nonpolar solvents. In methanol and in acetonitrile the aci-form is detected as a precursor of the anion; deprotonation occurs with first-order rate constants of ca.  $2 \times 10^5 \text{ s}^{-1}$  and ca.  $5 \times 10^4 \text{ s}^{-1}$  for the 2,4 and 2,6 compounds, respectively. The rates of intramolecular hydrogen abstraction in the lowest triplet states are estimated by comparison of the 2,4 and 2,6 triplet lifetimes with that of a model compound, 3,4-dinitrotoluene, for which there exists no channel of intramolecular hydrogen abstraction.

Etching of  $\text{SiO}_2$  by  $\text{CF}_3$  Radicals

N. Selamoglu, M. J. Rossi and D. M. Golden

Department of Chemical Kinetics

Chemical Physics Laboratory

SRI International

Menlo Park, CA



The Reaction of  $N_2O_5$  With Water on Carbonaceous Surfaces

L. Brower, M. J. Rossi and D. M. Golden

Department of Chemical Kinetics

Chemical Physics Laboratory

SRI International

Menlo Park, CA

POSTER SESSION E

The Shock Tube - Flash Photolysis - Resonance Absorption Technique for  
Measuring Bimolecular Rate Constants at High Temperatures

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Department of Applied Science  
Brookhaven National Laboratory  
Upton, New York 11973

An apparatus is described in which atomic species are produced by flash photolysis of the hot gas following compression by reflected shock waves. The absorbance of the atoms, so formed, is measured by resonance absorption spectroscopy, and decay constants of the transient atoms with selected reactants are measured under pseudo-first-order conditions. By working in the absorbance range where Beer's law is obeyed,  $\ln(\text{ABS}) = -k_{\text{obs}} t + c$ , and  $k_{\text{obs}} = k_{\text{bi}}[\text{R}]$ . Diffusion, the only other process by which atoms are lost from the detection zone, is too slow under nominal conditions to influence the kinetic behavior. Therefore,  $k_{\text{bi}}$  is determined unambiguously from a knowledge of  $[\text{R}]$  and of the temperature of the gas in the reflected shock region.

To date, reactions of H-atoms and O-atoms have been successfully investigated. However this technique can be extended to other atom and radical species. Data for the reactions,  $\text{H} + \text{NH}_3 \rightarrow \text{H}_2 + \text{NH}_2$  and  $\text{O} + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3$ , in the temperature range  $\sim 800\text{--}2000$  K, will be presented. These results will be compared to those of earlier studies, and the rate data for these reactions will be critically reviewed. The merits and the disadvantages of this technique will be fully discussed along with its general applicability to the study of the reactivity of other atomic and radical species at high temperatures.

\*This research was supported by the Division of Chemical Sciences, United States Department of Energy, Washington, D.C., under contract No. DE-AC02-76CH00016.

LASER PYROLYSIS/LASER FLUORESCENCE MEASUREMENTS  
OF HIGH TEMPERATURE OH REACTION RATES WITH  
PROPENE, BUTENES, AND AMMONIA\*

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We have developed a new method for studying bimolecular reactions at high temperatures and applied it to several OH reactions. The method of laser pyrolysis/laser fluorescence uses a pulsed CO<sub>2</sub> laser to heat a sample containing SF<sub>6</sub> absorber, CF<sub>4</sub> or N<sub>2</sub> bath gas, H<sub>2</sub>O<sub>2</sub> as a radical source, plus a reactant. Temperatures between 800 and 1400 K are attainable. Rate constants were measured by following the [OH] decay with time using laser induced fluorescence. Temperature and density measurements were made using the LIF itself. Fluorescence quenching measurements at high T were also made.

Despite a weak allylic CH bond, OH + C<sub>3</sub>H<sub>6</sub> shows no abstraction at lower temperatures. Our measurements reflect a new direct route at high T with moderate activation energy. The rate constant increases from  $4.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 960K to  $8.9 \times 10^{-12}$  at 1210K. RRKM calculations show that the low T addition channel no longer is significant. A variety of butene isomers will be examined to determine the nature of the abstraction barrier in these unsaturated hydrocarbons.

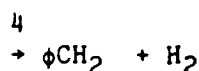
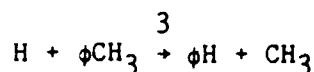
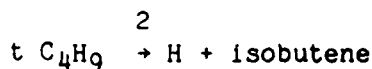
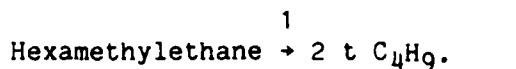
The OH + NH<sub>3</sub> rate constant ranges from  $3.4 \times 10^{-12}$  at 980K to  $6.4 \times 10^{-12}$  at 1425K. The curvature in the Arrhenius plot of this combined with other data at lower T can be explained in terms of transition state theory.

\* Supported by the Division of Basic Energy Sciences, Dept. of Energy,  
Contract DE-AC03-81ER10906

# Mechanism and Rate of Hydrogen Atom Attack on Toluene at High Temperatures

D. Robaugh and W. Tsang  
Chemical Kinetics Division  
National Bureau of Standards

Hexamethylethane has been decomposed in the presence of large excesses of toluene and methane/toluene mixtures in single pulse shock tube experiments in the temperature range 1000-1100K and at 2-5 atmos. Methane, ethane, isobutene and benzene are the main light hydrocarbon reaction products. At sufficiently high toluene/hexamethylethane ratio ( $\geq 100$  to 1) the main reactions are



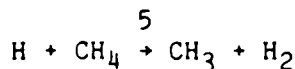
In the presence of toluene alone the relative yields of isobutene and benzene give a direct measure of  $k_4/k_3$  on the basis of the relation

$$k_4/k_3 = (\text{isobutene} - \text{benzene})/\text{benzene}$$

Using isobutene yields as an internal standard for the description of temperature conditions in the shock tube, we find

$$k_4/k_3 = 10^{1.0} \exp(-1660/T)$$

In the presence of sufficiently large quantities of methane, benzene yields are decreased. This is due to the competitive reaction



This leads to

$$k_5/k_3 = 10^{1.2} \exp(-4430/T)$$

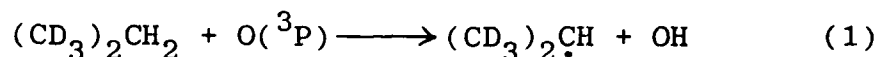
On the basis of our best estimate for  $k_5$ ,  $10^{11.4 \pm 0.3} \exp(-7050 \pm 500/T)$  l/mol-sec, in this temperature range, we find,  $k_3 = 10^{10.2 \pm 0.4} \exp(-2620 \pm 750/T)$  l/mol-sec,  $k_4 = 10^{11.2 \pm 0.4} \exp(-4280 \pm 750/T)$  l/mol-sec.

## Reaction of Propane and Isopropyl Radicals with Atomic Oxygen

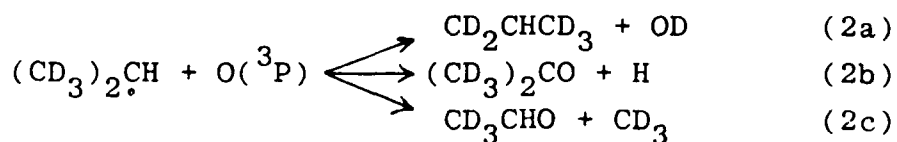
Nobuaki WASHIDA

The National Institute for Environmental Studies, P.O. Tsukubagakuen, Ibaraki 305 Japan

The reaction of oxygen atoms with 1,1,1,3,3,3-d<sub>6</sub>-propane, (CD<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>, in a fast-flow system was studied with a photoionization mass spectrometer. 1,1,1,3,3,3-d<sub>2</sub>-isopropyl radicals, (CD<sub>3</sub>)<sub>2</sub>CH, formed by the initial hydrogen abstraction at the 2-position were detected directly.



The subsequent reaction of (CD<sub>3</sub>)<sub>2</sub>CH radicals with atomic oxygen proceeds by both deuterium abstraction (61%) and an oxygen addition reaction (39%). The product in the deuterium abstraction was CD<sub>2</sub>CHCD<sub>3</sub> and those in the oxygen addition were (CD<sub>3</sub>)<sub>2</sub>CO (18%) and CD<sub>3</sub>CHO (21%).



Competition experiments show that (CD<sub>3</sub>)<sub>2</sub>CH radicals react (0.029 ± 0.004) times as fast with O<sub>2</sub> as with O(<sup>3</sup>P). In the presence of an excess of O<sub>2</sub>, CD<sub>2</sub>CHCD<sub>3</sub> was observed in decreased yield (20%) and (CD<sub>3</sub>)<sub>2</sub>CO and CD<sub>3</sub>CHO increased to 32 and 44%, respectively. The rate data for Reaction (1) were fitted by an Arrhenius expression:

$$k_1 = (2.0_{-0.7}^{+1.0}) \times 10^{-10} \exp[(-6086 \pm 392 \text{ cal mol}^{-1})/RT]$$

cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>. The rate of Reaction (1) obtained from the yields of products was 7.9 × 10<sup>-15</sup> cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup> at 298K.

## THE REACTION OF CYCLOPROPYL RADICALS WITH OXYGEN ATOMS

By

P. Heinemann, K. Hoyer mann

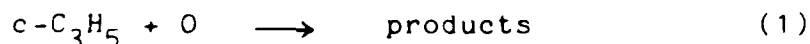
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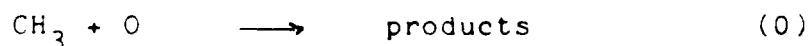
The reaction of cyclopropyl radicals with oxygen atoms was studied with respect to the rate constant and the primary reaction products at low pressure (<1 torr) and low temperature (<295 K).

The experimental set up consisted of two independent discharge flow tubes for the production of the radicals and atoms, a Laval nozzle reactor, a molecular beam sampling device and a mass spectrometer with synchronous single ion counting. The mass spectrometric identification of labile and stable species was accomplished via high resolution spectra and the measurement of ionization curves (detection of  $c\text{-C}_3\text{H}_5$ ,  $\text{CH}_3$  radicals at 14.5 eV). The  $\text{CH}_3$  and  $c\text{-C}_3\text{H}_5$  radicals were produced via H atom abstraction with F atoms.

The rate constant for the reaction

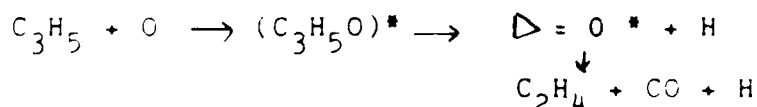


was measured relative to the reaction



$k_1/k_0 = 1.3 \pm (0.15)$ ; this is converted to  $k_1 = 1.1 \cdot 10^{14} \text{ cm}^3/\text{mol s}$  using the recommended value of  $k_0 = 8.3 \cdot 10^{13} \text{ cm}^3/\text{mol s}$ .

The main primary products of the reaction (1) were CO and  $\text{C}_2\text{H}_4$ . This is explained by the mechanism



(The detection of H atoms at  $m/e = 1$  was obstructed by the fragmentation of  $\text{C}_3\text{H}_5$  at  $m/e = 1$  in the electron impact ion source, the low mass spectrometric sensitivity of H atoms, and the loss of light species in the molecular beam used for sampling)

The contribution of other reaction channels ( $\text{CH} + \text{C}_3\text{H}_4$ ;  $\text{CH}_3 + \text{CH}_2\text{CO}$ ;  $\text{CH}_2\text{CCHO} + \text{H}$ ;  $\text{CH}_2 + \text{CH}_2\text{CO}$ ) to the total reaction is below 5 - 10%, based on the detection limit of the listed products.

The mechanism of the formation of H + cyclopropyl radicals is analogous to that of the alkyl + O reaction (2) (formation of H + allyl + acetylene; alkyl + allyl + acetylene). The subsequent decomposition

c-C<sub>3</sub>H<sub>4</sub>O\* in reaction (1) and the conservation of aldehyde/ketone in (2) is understood by the different activation energies of dissociation (130 kJ/mol and 230 - 300 kJ/mol, resp.). The dissociation products of c-C<sub>3</sub>H<sub>4</sub>O\* in reaction (1) (C<sub>2</sub>H<sub>4</sub> + CO) are the same as observed in the thermal and photochemical dissociation of c-C<sub>3</sub>H<sub>4</sub>O.



REACTIVITY TRENDS IN THE REACTIONS OF  $O(^3P)$  WITH ALCOHOLS AND KETONES

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The principal reaction path in the reaction of  $O(^3P)$  with alcohols is well established as abstraction of the hydrogen atom  $\alpha$ - to OH. We recently reported results for the temperature dependence of the rate constants for the reactions of  $O(^3P)$  with the butanols which demonstrated that CH bonds that were not  $\alpha$ - to OH contribute to the overall reactivity and that abstraction of such hydrogen atoms by  $O(^3P)$  occurs more readily than in the analogous alkanes.

The temperature dependence of the rate constants for the reactions of  $O(^3P)$  with acetone, 2-butanone and 3-pentanone has now also been measured in a discharge-flow system. The results are in excellent agreement with earlier experiments on acetone and with linear free energy predictions at 298K using recently reported kinetic data for the reactions of OH with ketones. The Arrhenius preexponential factors are smaller than for the reactions of  $O(^3P)$  with alcohols, even before correcting for the number of chemically equivalent hydrogen atoms, and are roughly two orders of magnitude smaller than those for the reactions of  $O(^3P)$  with alkanes. Extension of one alkyl group in the ketones from  $CH_3$  to  $C_2H_5$  (2-butanone) produces a large decrease in the activation energy while extension of the second alkyl group from  $CH_3$  to  $C_2H_5$  (3-pentanone) does not produce a significant further reduction in activation energy.

The data for the reactions of  $O(^3P)$  with alcohols and ketones are analysed using linear free energy relations. These results are compared with those of similar analyses of the reactions of  $O(^3P)$  with alkanes and aldehydes and of OH with the same four series of compounds.

The Arrhenius Parameters for the Reactions of Hydrogen and  
Oxygen Atoms with Five Fluoroethylenes

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The rate constants for the reactions of hydrogen and oxygen atoms with five fluoroethylenes have been measured over the temperature range 240-450 K, using a pulse radiolysis-resonance absorption technique. The Arrhenius parameters thus obtained were compared with those previously obtained for the reactions with  $C_2$ - $C_4$  hydrocarbon olefins. In the hydrogen atom reactions, the pre-exponential factors for the reactions with fluoroethylenes were found to be much smaller than those for hydrocarbon olefins. In the oxygen atom reactions, the pre-exponential factors changed by a factor of 4, first decreased with fluorine substitution and then increased again, so that the values for ethylene and tetrafluoroethylene were nearly the same. These findings will be discussed in terms of the transition state theory.

# Production and Reaction of the Isopropoxy Radical

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We report the first laser-induced fluorescence (LIF) and direct chemical kinetics measurements on the isopropoxy radical. Arrhenius parameters for its reaction with NO, NO<sub>2</sub>, and O<sub>2</sub> are obtained over the temperature range of 22 to 105°C. We have also made the first direct measurements of the temperature dependent unimolecular decomposition and measured the excitation spectrum over a 40 nm range (330-370 nm). The radical is prepared by 355 nm photolysis of isopropyl nitrite and probed by LIF via the A-X transition at 340 nm. With NO, the radical reacts via two channels: a bimolecular hydrogen abstraction and a termolecular combination reaction. The latter reaction predominates. We obtain a total isopropoxy disappearance rate constant of:

$$(9.30 \pm 1.29) \times 10^{-12} \exp(-0.81 \pm 0.09 \text{ kcal/mole/RT})$$

The reaction of isopropoxy radicals with O<sub>2</sub> to yield HO<sub>2</sub> and acetone is typical of alkoxy reactions. We obtain a rate constant of

$$(1.44 \pm 0.34) \times 10^{-14} \exp(0.355 \pm 0.146 \text{ kcal/mole/RT})$$

The temperature dependence of these systems will be compared with those of other alkoxy reactions. Alkoxy radicals are known to undergo thermal decomposition. This fact has been incorporated into kinetic modeling of hydrocarbon combustion systems. Few experimental measurements of this unimolecular decomposition have been made and none by direct means. The reaction is in the fall-off region at both 105 and 133°C using between 1 and 400 Torr N<sub>2</sub> as a buffer gas.

\*NRC/NRL Postdoctoral Research Associate

KINETICS OF THE ISOTOPE EXCHANGE  
REACTION OF  $^{18}\text{O}$  WITH NO AND  $\text{O}_2$  AT 298 K

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Recent experimental and theoretical results for the high pressure rates of association of O with NO and  $\text{O}_2$ <sup>1</sup> are larger than those derived from early isotope exchange rate measurements.<sup>2,3</sup> We have conducted experiments on both systems using a new discharge-flow/modulated molecular beam mass spectrometer apparatus. Detection limits for NO,  $^{16}\text{O}$ , and  $^{18}\text{O}$  were  $2 \times 10^9$ ,  $2 \times 10^{10}$ , and  $6 \times 10^{10}$ , respectively, using 20 eV electrons. High sensitivity allowed small reactant concentrations ( $[^{18}\text{O}] = 1.5 \times 10^{12}/\text{cc}$ ) which minimized the effects of secondary scrambling reactions.

For the  $^{18}\text{O} + \text{N}^{16}\text{O} \leftrightarrow ^{16}\text{O} + \text{N}^{18}\text{O}$  exchange, reaction times were kept short to avoid reconversion of product  $^{16}\text{O}$  to  $^{18}\text{O}$  by undissociated  $^{18}\text{O}_2$ . The effect of this process at longer times is discussed, and it is shown that [NO] can serve as a probe to study the  $^{16}\text{O} + ^{18}\text{O}_2 \rightarrow ^{18}\text{O} + ^{18}\text{O}^{16}\text{O}$  reaction. Direct measurements of the  $^{16}\text{O} + ^{18}\text{O} \leftrightarrow ^{18}\text{O} + ^{18}\text{O}^{16}\text{O}$  exchange yielded a rate constant close to that obtained from the NO experiments.

Our result for the O + NO exchange,  $k_1^X = (3.7 \pm 0.5) \times 10^{-11}$  cc/s, implies  $k_1^{\infty} = (7.4 \pm 1.0) \times 10^{-11}$ , above the  $3.0 \times 10^{-11}$  obtained by Hippler et al. in high pressure experiments,<sup>4</sup> close to recent theoretical estimates which give  $k_1^{\infty} = 5.6 \times 10^{-11}$ ,<sup>5</sup> and equal to that suggested by the vibrational relaxation experiments of Fernando and Smith,<sup>6</sup>  $k_1^{\infty} = (7.5 \pm 0.5) \times 10^{-11}$  cc/s.

For the O +  $\text{O}_2$  exchange, we obtain a forward rate constant of  $k_2^X = (3.3 \pm 0.8) \times 10^{-12}$  cc/s, three times larger than the results of the early studies<sup>2,3</sup> and the trajectory calculations of Varandas and Murrell.<sup>7</sup> The result of Jaffe and Klein,  $k_2^X = 1.7 \times 10^{-12}$ ,<sup>8</sup> is somewhat closer to our value. Our  $k_2^X$  implies  $k_2^{\infty} = ((3.3-6.6) \pm 1.6) \times 10^{-12}$ , depending on whether the exchange occurs by direct collision or complex formation. These may be compared with Hippler and Troe's experimental value of  $k_2^{\infty} = 2.8 \times 10^{-12}$ ,<sup>9</sup> and Quack and Troe's theoretical estimate,  $k_2^{\infty} = 6.3 \times 10^{-12}$ .<sup>10</sup>

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A KINETIC STUDY OF THE REACTION  $\text{OH} + \text{HNO}_3 + \text{M}$

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Absolute rate constants for the reaction of OH radicals with  $\text{HNO}_3$  have been determined over a range of  $\text{HNO}_3$  concentrations at 296K and at total pressures of 1-16 torr  $\text{HNO}_3$ , 500 torr  $\text{N}_2$ , and 600 torr  $\text{SF}_6$ . Hydroxyl radicals were generated by laser flash photolysis of  $\text{HNO}_3$  at 222 nm (KrCl excimer laser line) and were monitored in absorption by time resolved attenuation of the OH resonance radiation at 308.15 nm.  $[\text{OH}(\text{A}^2\Sigma^+ - \text{X}^2\Pi)]$ .

The  $\text{HNO}_3$  concentration was determined continuously in the cell spectrophotometrically at 210 nm. The  $\text{NO}_2$  in  $\text{HNO}_3$  was also determined spectrophotometrically at 405 nm (where  $\text{HNO}_3$  does not absorb) before and after the rate measurement.  $\text{HNO}_3$  was always found to contain (0.1-0.2)%  $\text{NO}_2$ .

It was established by numerical simulation that whereas the  $\text{NO}_2$  impurity did not influence the measured rate constants at low total pressure it did increase their value by up to 20% at high pressures of  $\text{N}_2$  and  $\text{SF}_6$ . The individual values of the rates at these pressures were corrected for the contribution of  $\text{NO}_2$  using the well established values of the rate constants of  $\text{NO}_2 + \text{OH} + \text{M}$ , for  $\text{N}_2$  and  $\text{SF}_6$ . The resulting second-order rate constants in  $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$  are:

1-16 torr $\text{HNO}_3$ ,	$k = 7.56 \pm 0.45 \times 10^{10}$
500 torr $\text{N}_2$ ,	$k = 7.20 \pm 0.47 \times 10^{10}$
600 torr $\text{SF}_6$	$k = 8.41 \pm 0.48 \times 10^{10}$

The quoted uncertainties are the 95% confidence levels. Any potential systematic error due to the error in the  $\text{NO}_2$  determination and the applied corrections is estimated to be  $\pm 10\%$ .

Conclusions. Our rate constant at low pressure agrees very well with the higher value reported in several recent determinations. There is no significant pressure effect on the rate constant, although a small effect of about 10% bordering the experimental error can not be excluded.

THE ROLE OF SELECTIVITY FOR RADICAL ABSTRACTION OF HYDROGEN ATOMS  
IN THE OXIDATION OF NORMAL AND ISOPROPYLBENZENE

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Experimental results from the oxidation of normal and isopropylbenzene in the Princeton flow reactor at atmospheric pressure and  $\sim 1050$  K are presented. For the conditions of the experiments the pool of H, O, and OH grows rapidly, and radical abstraction of hydrogen atoms from the sidechain is the dominant reaction for fuel consumption. The various hydrocarbon radical species formed by abstraction are found to react quickly to form stable species with olefinic sidechains or benzyl radicals. Thus, the initial task in the analysis of the experimental data is to explain the product distribution resulting from the abstraction of benzylic, primary or secondary hydrogens in the sidechain. In the analysis of the isopropylbenzene results quantitative information is obtained on the selectivity for benzylic hydrogen abstraction relative to primary hydrogen abstraction.

For normal propylbenzene the data show major products indicative of the abstraction of benzylic and primary hydrogens but much smaller amounts of species which would form after abstraction of a secondary hydrogen. The relatively small amounts of the products from secondary hydrogen abstraction suggest that the radical formed may undergo a 1-2 hydrogen shift to the more stable benzylic radical. Such a shift reaction is possible because the competing reaction of hydrogen elimination is relatively slow.

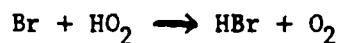
For isopropylbenzene the data indicate a simpler product distribution from fuel consumption primarily because only benzylic and primary hydrogens are present. The two major products, styrene and  $\alpha$ -methylstyrene, are explained by decomposition of the hydrogen radicals formed through the abstraction of primary and benzylic hydrogens respectively. Because two distinct products are formed as a result of the abstractions, an overall selectivity for the abstraction of a benzylic hydrogen relative to a primary hydrogen can be obtained from the data.

Reaction Kinetics of  $\text{Br} + \text{HO}_2 \rightarrow \text{HBr} + \text{O}_2$

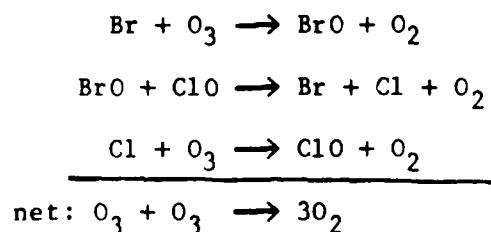
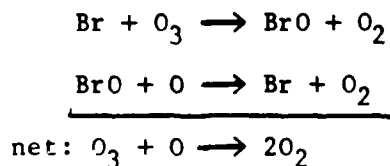
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The reaction of bromine atoms with the hydroperoxyl radical



could be an important sink for stratospheric bromine. In the stratosphere, Br behaves much like Cl, destroying odd-oxygen species (odd-oxygen =  $\text{O}_3 + \text{O}$ ) through the catalytic cycles:



Hence, the  $\text{Br} + \text{HO}_2$  reaction reduces the effective destruction of ozone by bromine. Preliminary experiments in this laboratory indicate that the rate

constant for this reaction may be significantly larger than earlier reported;<sup>1,2</sup> therefore, a thorough characterization of the title reaction was recently initiated. This study, employing a discharge flow reactor with laser magnetic resonance detection of HO<sub>2</sub> and resonance absorption detection of Br, is the first determination of the rate constant of the title reaction using multiple atom and radical sources and simultaneous detection of both species. The rate constant for the title reaction, its temperature dependence, and the implications for stratospheric ozone destruction by bromine will be discussed.

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KINETICS OF GAS PHASE REACTIONS OF  $\text{SiF}_2$ 

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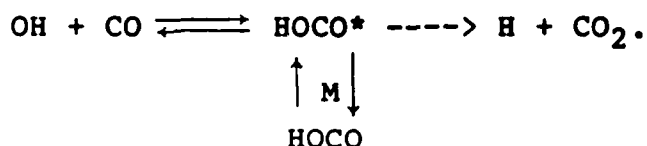
Reactions of silicon difluoride radicals are of interest in studies of the mechanisms of silicon etching in fluorine-containing plasmas, because  $\text{SiF}_2$  may be a primary desorption product or a major surface species. We have studied the reactions of  $\text{SiF}_2$  with  $\text{F}_2$ , atomic fluorine,  $\text{O}_2$ , and  $\text{H}_2$  in a room temperature discharge flow system.  $\text{SiF}_2$  is prepared in an oven source either by decomposition of  $\text{SiF}_4$  over silicon at  $T \approx 1100^\circ\text{C}$  or by decomposition of  $\text{Si}_2\text{F}_6$  at  $T > 700^\circ\text{C}$ . Fluorine atom concentrations, produced by microwave discharge in  $\text{F}_2/\text{He}$  mixtures, are measured by titration with  $\text{Cl}_2$  and by tunable diode laser absorption. Laser induced fluorescence excited at 221 nm is used to measure pseudo first order decay of  $\text{SiF}_2$  in the presence of excess reactant. No reaction is noted with  $\text{O}_2$  or  $\text{H}_2$  ( $k < 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ ). Preliminary results for the reaction of  $\text{SiF}_2$  with  $\text{F}_2$  suggest a rate constant on the order of  $k \approx 5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ .

# KINETIC AND MECHANISTIC STUDIES OF THE OH + CO REACTION

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The reaction of OH with CO plays a major role in atmospheric and combustion chemistry. Numerous investigations of this reaction are reported in the literature, and it is now clear that reaction proceeds via a complex mechanism:



In the presence of relatively efficient third bodies such as N<sub>2</sub>, O<sub>2</sub>, CF<sub>4</sub>, and SF<sub>6</sub>, the overall rate constant for OH removal is known to increase with pressure. However, the exact magnitude of the pressure dependence in N<sub>2</sub> and O<sub>2</sub> is not known with sufficient accuracy for purposes of atmospheric modelling. Also, the fate of the HOCO radical in laboratory systems and in the real atmosphere is not well documented.

We are currently investigating two aspects of the OH + CO reaction. A pulsed laser photolysis-pulsed laser induced fluorescence apparatus is being employed to obtain direct, real time measurements of OH kinetics in air at pressures up to 1 atm and as a function of temperature. In a separate set of experiments, 157 nm pulsed laser photolysis of H<sub>2</sub>O is being employed in conjunction with resonance fluorescence detection of H and laser induced fluorescence detection of OH to measure the H atom yield as a function of pressure over the range 50-800 Torr N<sub>2</sub>. The results of these experiments will be presented and their implications for atmospheric chemistry and our basic understanding of the reaction mechanism will be discussed.

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# The Temperature Dependence of Reactions of the SO Radical

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The reaction kinetics of ground state SO  $X^3\Sigma$  free radicals have been studied in a discharge flow system near 1 Torr over a temperature range of 210–400 K. Ground state SO radicals were generated by a microwave discharge in dilute SO<sub>2</sub>/He mixture. S and O atoms impurities were removed using a discharge bypass technique. Concentrations of free radicals were determined using collision free sampling to a quadrupole mass spectrometer.

Pseudo first order kinetics, with  $[SO]_0 \ll [X]_0$ , were used to determine rate constants for the reactions



and with  $[SO]_0 \gg [X]_0$  for the reaction



Absolute calibration of the SO signal was determined by chemical titration with NO<sub>2</sub>, while absolute calibration of ClO and BrO signals was accomplished by chemical titration with NO. The results presented will be discussed with those previously reported.

Photoionization/Electron Cyclotron Resonance Detection  
of Gas Phase Radicals

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Electron paramagnetic resonance (EPR) detection of atoms and diatomic radicals has been employed in numerous gas phase kinetics studies, but this technique is not sufficiently sensitive to detect radicals that have more than three atoms. We will describe a new technique for detecting polyatomic radicals that utilizes EPR instrumentation but is not based on paramagnetic resonance. In this method, electron cyclotron resonance absorption is used to detect free electrons that are produced by selective photoionization of free radicals. Results for NO and CF<sub>3</sub> radical detection will be presented. The current lower detection limit for these species is about  $2 \times 10^{10} \text{ cm}^{-3}$ .

This technique is being used to study kinetics of radical-radical reactions involving CF<sub>3</sub> radicals. Our latest results for the reactions,



will be presented.

"Laser Induced Fluorescence Study of Pulsed Laser Photolysis  
of Acetaldehyde and Kinetics of HCO"

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HCO ( $\tilde{X}^2A'$ ) radicals have been produced by an excimer laser photolysis of  $CH_3CHO$  at 308 nm and the kinetics of HCO radicals have been studied by the pulsed dye laser excitation of the HCO ( $\tilde{A}^2A''$ ) fluorescence at 614.46 nm.<sup>1</sup> Since the predissociation of HCO ( $\tilde{A}^2A''$ ) is dominant, the fluorescence signal is extremely weak. The LIF emission spectrum from the HCO ( $\tilde{A}^2A''$ ) in the  $09^0_0$  level has been wavelength resolved. The fluorescence decay time

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$\lambda_{em}$ (nm)	658.2	708.0	722.4	764.0	781.4
$v_1''v_2''v_3''$	(010)	(020)	(100)	(030)	(110)

---

of HCO ( $\tilde{A}^2A''$ ) was  $\leq 15$  nsec at 5 torr  $CH_3CHO$  pressure. Our lifetime value is shorter than the 46 nsec lifetime reported by König and Lademann<sup>2</sup> and we do not observe the 644 nm emission they reported. A study of the LIF intensity vs the delay time between the photolysis pulse and the probe laser pulse shows that the HCO disappearance follows second order kinetics (in HCO). The details will be presented.

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\*This research has been supported by the NSF Grant CHE-82-17121.

The Photochemistry and Kinetics of Butadiyne  
in the Atmosphere of Titan

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The butadiyne photodecomposition mechanism and subsequent rates of reaction of the free radicals produced are of importance to the chemistry of Titan's atmosphere. This information is required to determine the validity of a proposed model by which condensible products are produced by  $C_2H$  and  $C_4H$  radical reaction with the parent compound and other materials found in Titan's atmosphere. Since the model involves a range of wavelengths, the photolysis of butadiyne has been studied at four wavelengths in the region of interest (147 to 254 nm). Product analysis resulting from the photodecomposition of butadiyne alone and in the presence of a large excess of deuterium showed the presence of free radicals at 185 and 147 nm. Both  $C_2HD$  and  $C_4HD$  were identified by mass spectral analysis. At the longer wavelengths used (228 and 254 nm) the isotope technique indicated an absence of free radical reactions.

The importance of  $C_2H$  and  $C_4H$  radicals in planetary chemistry lies in their rates of reaction with various constituents in its atmosphere. While some information is available in the formation and reaction of the  $C_2H$  radical, little is known about the kinetics of  $C_4H$  radical reactions. The present results suggest that photolysis of  $C_4H_2$  is a convenient source of  $C_4H$  and that relative rate constants for reaction of  $C_4H$  could be obtained using the same techniques of isotopic labeling and mass spectrometric analysis of stable products. It would be of value to determine rate constants for the reaction of  $C_4H$  with hydrogen, alkanes, alkenes, and alkynes.

## KINETICS OF METHYLPEROXY RADICAL DESTRUCTION BY NO, USING DFMS

by G. L. Pellett and B. R. Adams  
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This paper presents heretofor unpublished results on rate coefficients and reactive intermediates obtained from a low-pressure microwave-discharge flow reactor (DFR) operated at ambient temperature. A three-stage modulated molecular beam sampling system, coupled to a quadrupole mass spectrometer and mutually slaved (with respect to beam modulation) to a digital data processing system, was used to monitor reactants and products over relatively wide ranges of concentration, reaction length (times), and pressure.

Methylperoxy radical was prepared during the main part of the study by reacting Cl-atom (from 1% Cl<sub>2</sub> in He) with a He-diluted mixture of CH<sub>4</sub> and O<sub>2</sub>. Systematic exploratory studies were conducted with both He and Ar diluent over feasible ranges of Cl<sub>2</sub>, CH<sub>4</sub>, and O<sub>2</sub> concentration in order to optimize CH<sub>3</sub>OO• production while minimizing undesirable secondary reaction effects. Similar efforts were focused on evaluating the effects of sequential addition of CH<sub>4</sub> and O<sub>2</sub>, and systematic variation of reactor pressure and residence time, in efforts to determine if certain anticipated complications were important: i.e., reformation of Cl-atom via ClOO• + Cl + O<sub>2</sub>; formation of CH<sub>3</sub>O• via partially nonterminating CH<sub>3</sub>OO• recombination, followed by CH<sub>3</sub>O• + O<sub>2</sub> + HOO• + CH<sub>2</sub>O and subsequent consumption of CH<sub>3</sub>OO• by HOO• and CH<sub>3</sub>O•. Selected results from these and other supporting mass spectral surveys will be presented.

Pseudo first order kinetic conditions were used to determine a rate coefficient,  $k = 6.3 \pm 0.3 \times 10^{-12} \text{ cm}^3/\text{molec-s}$  for production of NO<sub>2</sub> attributed to CH<sub>3</sub>OO• + NO + NO<sub>2</sub> + CH<sub>3</sub>O•. The  $k$  represents an average from 11 sets of 191 runs (total), using three different NO mixtures. Helium was used as diluent; average pressure was 2 torr; and temperature was 298 °K. Three of these sets were obtained using <sup>15</sup>NO, which led to direct evidence (absence of HONO) that CH<sub>3</sub>OO• + NO + HONO + CH<sub>2</sub>O was not a significant pathway for CH<sub>3</sub>OO• destruction. Details of the above results will be presented in combination with additional mass spectral evidence supporting the presence/absence of several postulated intermediates and final products.

# A Direct Kinetic Study of the Reaction $\text{Cs} + \text{I} + \text{He} \longrightarrow \text{CsI} + \text{He}$ ,

by D.Husain, J.M.C. Plane and Chen Cong Xiang.

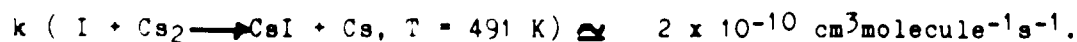
We have investigated this reaction by monitoring the concentration of  $\text{I}(^2\text{P}_{3/2})$  by time-resolved resonance fluorescence spectroscopy [  $\text{I}(6^2\text{P} - 5^2\text{P}_{3/2})$ ,  $\lambda = 178.3 \text{ nm}$  ]. The  $\text{I}(^2\text{P}_{3/2})$  atoms are produced by flash photolysis of  $\text{CsI}$  vapour in a known excess of  $\text{Cs}$  and  $\text{He}$ , so that the loss of  $\text{I}(^2\text{P}_{3/2})$  is pseudo-first-order with respect to the other reactants.

The source of  $\text{Cs}$  vapour is a heat-pipe oven coupled to the high-temperature reaction cell, from where the metal is entrained in a flow of helium. The concentration of  $\text{Cs}$  is monitored by steady atomic resonance fluorescence spectroscopy [  $\text{Cs}(7^2\text{P}_J - 6^2\text{S}_{1/2})$ ,  $\lambda = 451 \text{ nm}$  ], with phase sensitive detection.  $\text{CsI}$ , the precursor of  $\text{I}$  atoms, is produced in situ in the reaction cell by reaction of a trace of  $\text{CH}_3\text{I}$  with the  $\text{Cs}$  vapour from the heat-pipe.

We report the following rate constant:

$$k(T = 491 \text{ K}) = 7.9 \pm 1.2 \times 10^{-31} \text{ cm}^6 \text{molecules}^{-2} \text{s}^{-1}.$$

This rapid atom-atom recombination rate is discussed in the context of shock-tube studies on the thermal dissociation of  $\text{CsI}$ , as well as atomic beam studies of collisional ionisation of the alkali halides. Monte-Carlo calculations are performed to model the rate over a range of temperature. The effect of the low probability of the reaction successfully following an adiabatic channel involving charge transfer is analysed, particularly with regard to the early fall-off behaviour of this reaction from third to second order with increasing pressure of the third body. Finally, a rough estimate is obtained for the reaction of  $\text{I}(^2\text{P}_{3/2})$  with the cesium dimer:





# Rate Coefficients for the $\text{CH}_3\text{SH}-\text{NO}_2$ Reaction

by

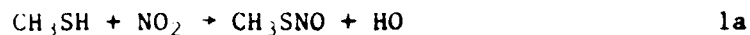
R. Jeffrey Balla and Julian Heicklen

Department of Chemistry and Communications & Space Science Laboratory  
The Pennsylvania State University, University Park, Pa., 16802

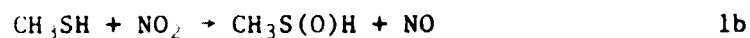
The thermal reaction between  $\text{CH}_3\text{SH}$  and  $\text{NO}_2$  was studied at 296-458 K by monitoring  $\text{NO}_2$  disappearance in a large excess of  $\text{CH}_3\text{SH}$ . The second-order reaction rate coefficient was independent of total pressure. The Arrhenius plot is best fitted by the sum of two exponentials:

$$k_1 = 3.2 \times 10^{-16} \exp(-4300/T) + 2.0 \times 10^{-9} \exp(-10,300/T) \text{ cm}^3/\text{sec}$$

where  $k_1$  is the rate coefficient for  $\text{NO}_2$  removal by  $\text{CH}_3\text{SH}$ . The first and second terms on the right-hand side of the expression presumably apply, respectively, to the four center reaction



and to the atom-transfer exchange reaction



Laser Measurement of the Rate Constants  
for Reaction of CN Radical with Hydrocarbons

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The gas phase bimolecular rate constants for the reaction of CN radicals with a number of saturated and unsaturated hydrocarbons have been determined at 300 K. The effects of vibrational excitation of CN radicals on the rate constants have also been investigated for various hydrocarbons.

Table 1 summarizes the bimolecular rate constant for different hydrocarbons. As shown in Table 1, the reaction rate for most hydrocarbons are very fast and near gas kinetic. We also find that the vibrational energy has little effect on the reaction rate of CN with different hydrocarbons.

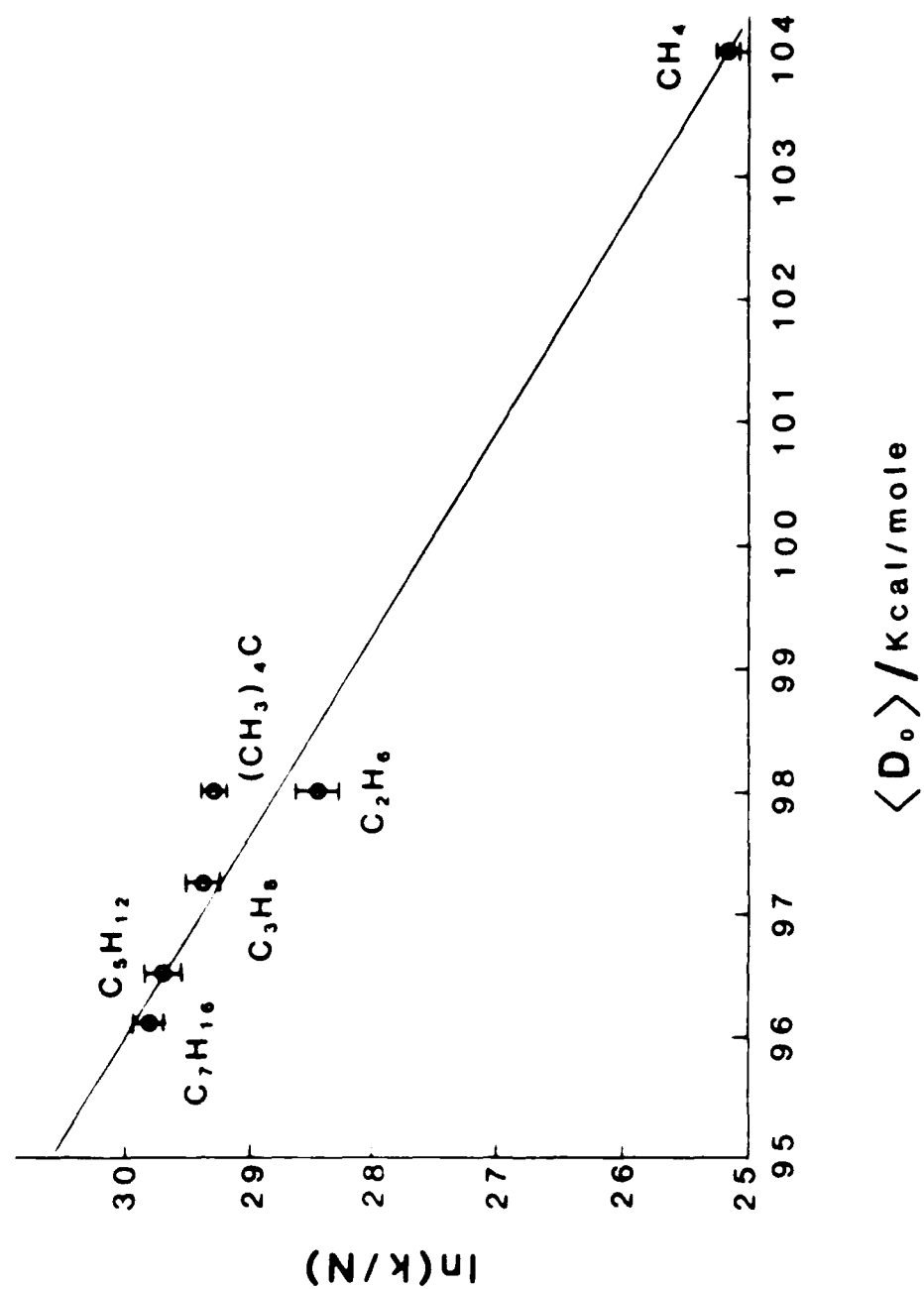
As shown in Figure 1, a linear correlation was found to exist between the logarithm of the rate constant per C-H bond and the corresponding bond dissociation energy for saturated hydrocarbons, but for unsaturated hydrocarbons, no such correlation could be found.

The reaction rate of CN with alkenes and alkynes is higher considerably compared to alkanes. Since these unsaturated hydrocarbons contain more reaction  $\pi$  bond, their reaction rates are expected to be higher than those predicted on the basis of the number of C-H bonds and their average bond strength.

Theoretically calculations are on the way to find out why the reaction rate is so fast for these hydrocarbons.

Table 1

The Bimolecular Rate Constants of $CN(v^n)+M \rightarrow \text{Products}$				
M	Vibrational Level	$k$ ( $\text{cm}^3/\text{molec.s}$ )	Literature's values	Ref.
$\text{CH}_4$	$v^n=0$	$(5.6 \pm 0.3) \times 10^{-13}$	$(5 \pm 3) \times 10^{-13}$	Ber. Bun. Phys. Chem. <u>81</u> 6701 (1977)
	$v^n=1$	$(8.4 \pm 0.3) \times 10^{-13}$	$(8.4 \pm 0.3) \times 10^{-13}$	J.C.S. Faraday Trans. 1 <u>68</u> , 2175 (1972)
$\text{C}_2\text{H}_6$	$v^n=0$	$(2.3 \pm 0.2) \times 10^{-11}$	$(3.0 \pm 0.1) \times 10^{-11}$	M.C. Lin Private Communication
	$v^n=1$	$(2.5 \pm 0.2) \times 10^{-11}$		
$\text{C}_3\text{H}_8$	$v^n=0$	$(8.1 \pm 1.0) \times 10^{-11}$		
	$v^n=1$	$(8.7 \pm 1.0) \times 10^{-11}$		
$\text{C}_5\text{H}_{12}$	$v^n=0$	$(1.6 \pm 0.2) \times 10^{-10}$		
	$v^n=1$	$(1.6 \pm 0.2) \times 10^{-10}$		
$\text{C}_7\text{H}_{16}$	$v^n=0$	$(2.3 \pm 0.2) \times 10^{-10}$		
	$v^n=1$	$(2.6 \pm 0.3) \times 10^{-10}$		
$(\text{CH}_3)_4\text{C}$	$v^n=0$	$(1.1 \pm 0.1) \times 10^{-10}$		
	$v^n=1$	$(1.1 \pm 0.1) \times 10^{-10}$		
$\text{CH}_3\text{OH}$	$v^n=0$	$(1.2 \pm 0.2) \times 10^{-11}$		
	$v^n=1$	$(1.3 \pm 0.2) \times 10^{-11}$		
$\text{C}_2\text{F}_4$	$v^n=0$	$(2.5 \pm 0.3) \times 10^{-11}$		
	$v^n=1$	$(2.6 \pm 0.3) \times 10^{-11}$		
$\text{C}_2\text{F}_3\text{H}$	$v^n=0$	$(4.2 \pm 0.3) \times 10^{-11}$		
	$v^n=1$	$(4.6 \pm 0.3) \times 10^{-11}$		
$\text{C}_2\text{H}_4$	$v^n=0$	$(2.1 \pm 0.2) \times 10^{-10}$	$(2.8 \pm 0.1) \times 10^{-10}$	M.C. Lin Private communication
	$v^n=1$	$(2.3 \pm 0.2) \times 10^{-10}$		
$\text{CH}_3\text{C}_2\text{H}$	$v^n=0$	$(2.1 \pm 0.5) \times 10^{-10}$		
	$v^n=1$	$(2.3 \pm 0.5) \times 10^{-10}$		
$\text{C}_2\text{H}_2$	$v^n=0$	$(2.2 \pm 0.2) \times 10^{-10}$	$(2.4 \pm 0.1) \times 10^{-10}$	M.C. Lin Private communication
	$v^n=1$	$(2.2 \pm 0.2) \times 10^{-10}$		
	$v^n=2$	$(2.4 \pm 0.3) \times 10^{-10}$		



# The Reactions of $O_2$ and $HO_2$ with $CH_2OH$ Radicals

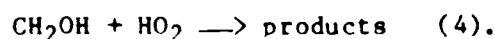
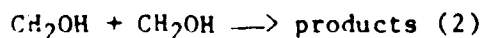
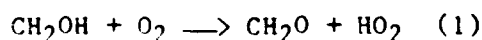
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In earlier works [1,2] the rate coefficient ( $k_1$ ) of the reaction  $CH_2OH + O_2 \rightarrow HO_2 + CH_2O$  was deduced by measurement of the product  $HO_2$ . We, therefore, undertook a discharge flow study in which  $CH_2OH$  radicals were directly measured by an electron impact mass spectrometer at ionization energies below 10 eV. The reaction  $CH_3OH + Cl$  was used as a  $CH_2OH$  source and was shown to be "clean". The usable concentration range was small:  $0.8 \cdot 10^{12} \text{ cm}^{-3} \leq [CH_2OH]_0 < 4 \cdot 10^{12} \text{ cm}^{-3}$ , the upper limit being determined by the fast gas phase recombination reaction of  $CH_2OH$ .

We measured exponential  $CH_2OH$  decay curves that were pseudo-first-order, and values were obtained for  $4 \cdot 10^{12} \text{ cm}^{-3} \leq [O_2]_0 \leq 50 \cdot 10^{12} \text{ cm}^{-3}$  with a resultant observed bimolecular rate constant of  $k_{obs} = (1.03 \pm 0.08) \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  at 298 K. The relation between  $k_1$  and  $k_{obs}$  is mainly given by the reactions:



Measurement of  $CH_2OH$  decays in the absence of  $O_2$  led us to  $k_3 = 10 \text{ s}^{-1}$  and  $k_2 = 1.5 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . The contribution of reaction 4 depends on  $[CH_2OH]_0$  as well as  $[O_2]$ . We therefore measured  $HO_2$  (33 amu) at a fixed time of 6 ms as a function of  $[CH_2OH]_0$  and  $[O_2]$ . Ethyleneglycol (product of reaction 2) fragments at 33 amu, and therefore corrections had to be made for  $HO_2$ . Comparison of the measured  $HO_2$  curves with simulated ones yield  $k_4 = 6 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (uncertainty factor 2). This in turn allows  $k_1$  to be deduced from  $k_{obs}$ :  $k_1 = (9.5 \pm 2.5) \cdot 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , and this value is in large discrepancy to currently accepted values.

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## Gas Phase Oxidation Chemistry of Sodium

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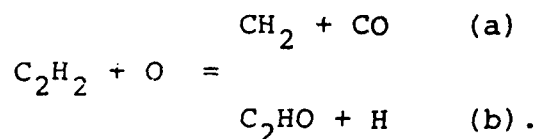
The oxidative chemistry of sodium plays a significant role in combustion corrosion processes, flame suppression, emissions from the lower thermosphere, and may be important in the stratosphere by affecting ozone reduction via the catalytic chlorine cycle. Our understanding of these processes is hampered by a lack of kinetic data. We will discuss the results of an ongoing experimental program to measure the reaction rate constants and photodissociation cross sections which are most important to these problems.

Rate constants for the reactions of interest are measured in a fast flow reactor, detecting atomic sodium by laser-induced fluorescence. Sodium oxide and hydroxide species are formed using a variety of chemical reactions, and their concentrations during reaction are followed by converting them back to atomic sodium in the detection region of the flow tube via chemical titration. In this presentation, we will report the results for the reaction rate constants of  $\text{Na} + \text{O}_3 \rightarrow \text{NaO} + \text{O}_2$  and  $\text{NaO}_2 + \text{HCl} \rightarrow \text{NaCl} + \text{HO}_2$ . The impact on atmospheric and combustion processes of these and other alkali reactions which we have investigated will be discussed.

A NEW LOOK AT HIGH TEMPERATURE  $C_2H_2/O$ -SYSTEM INCORPORATING  
RECENTLY OBTAINED INFORMATION ON METHYLENE KINETICS

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Reactions of acetylene form an essential subsystem in the oxidation of many hydrocarbons under both rich and lean flame conditions. There has been a controversy in the literature as to the reaction products of the primary step:

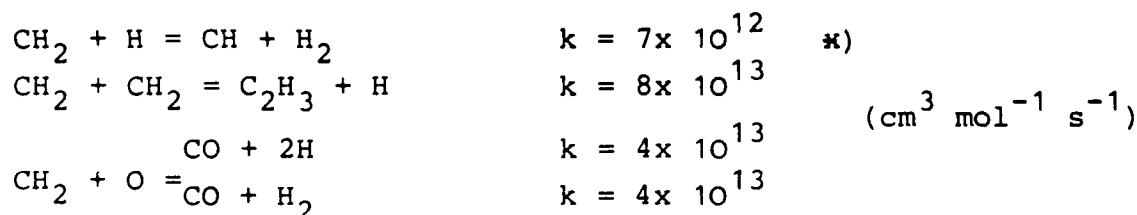


Jones and Bayes (1) found a contribution of 15 to 50 % for channel (a), Harding (2) showed by theoretical considerations, channel (b) to be dominant, whereas Hoyermann et al (3) gave experimental evidence that channel (a) contributes 95 %. Most of the numerous experimental investigations were restricted to low temperatures, with only a few studies at high temperatures (4,5).

At high temperatures it is to be expected that an investigation of  $C_2H_2 + O =$  products will be affected by the very fast subsequent reactions of  $CH_2$ . The latter had been recently investigated by extensive shock tube experiments (6). A reinvestigation of  $C_2H_2 + O =$  products seems to be justified, because the earlier experiments of Boehr and Roth (4) could be evaluated by them only with some assumed rate coefficients for the  $CH_2$  system. A series of shock tube measurements on  $C_2H_2/N_2O$  mixtures were carried out covering the temperature range  $1700 < T < 2500$  K and total pressure  $1.5 < p < 2.0$  bar. Atomic oxygen laser resonance absorption spectrometry was used for the simultaneous monitoring of the species H and O or CO. Making use of the high temperature methylene kinetics data obtained earlier (6) a reaction scheme was established, and simulation of the measured profiles lead to the following conclusions:

- i) Channel (b) is faster than reported by Loehr and Roth (4) by a factor of 1.5
- ii) Channel (a) is slower than channel (b) in the investigated temperature range. The determination of its rate coefficient however is less accurate. Channel (a) contributes about 40 % to the total reaction.
- iii) Channel (b) being faster than channel (a) is in agreement with theoretical predictions of Harding (2).
- iv) Attempts are under way to explain the low temperature  $C_2H_2/O/H$  measurements of Homann et al (5), under the assumption that the branching ratio for  $C_2H_2 + O$  as found at high temperatures may be approximately the same at room temperature in accordance with Jones and Bayes (1). Homann in his work considered only channel (a) to be dominant up to 500 K.

In arriving at the above conclusions, high temperature methylene oxidation kinetics (6) play a significant role. The dominating reactions were:



\*) = The rate coefficient of this reaction around 2000 K is definitely lower than the value at room temperature as reported recently by Boehland and Temps (7).

From our modeling an attempt is made to extract some quantitative values for high temperature reactions of the ketyl radical, which is produced by reaction (b).

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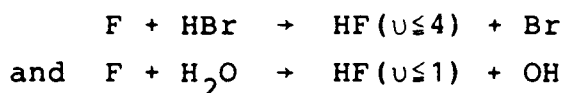
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- 

+ ) on sabbatical leave from the Indian Institute of Technology, Madras, India

# Measurement of Vibrational Groundstate Populations of HF Formed in F-Atom Reactions

by H. Heydtmann and J. Fendel  
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IR chemiluminescence is a well know tool to study the relative population of vibrational and rotational states of several diatomic species formed in elementary gas phase processes. In our laboratory the reactions



have been studied with this method. It is highly desirable to have information of the groundstate populations which cannot be obtained in this way. We therefore have buildt an HF-CW Laser and habe probed the two reaction systems in two configurations. In the first experiments the Laser beam passed the reaction volume twice. The 1P4, 1P5, 2P3 and 2P5 lines were used. About 1 Watt was achieved for each transition. Enhanced IR emission was expected but the increase in signal was too small for quantitative population evaluations. Successful, however, was the second configuration in which the reaction volume was placed intracavity. For the reaction  $\text{F} + \text{H}_2\text{O}$  fluorescence signals could be observed enhancing the ordinary emission from chemiluminescence. Another possibility is to monitor directly the Laser power in the single line operation. Inversion between the  $\text{HF}(v=1, J=3)$  and the  $\text{HF}(v=0, J=4)$  states is shown to be present in the  $\text{F} + \text{H}_2\text{O}$  system but not in the  $\text{F} + \text{HBr}$  system under our experimental conditions. IR chemiluminescence results for the two reactions are discussed together with the new information obtained.

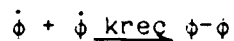
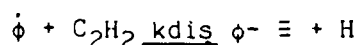
Rate Constants for Reactions of Phenyl Radicals  
with Acetylene, Ethylene and Benzene

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While phenyl radicals are probable intermediates in pyrolysis reactions leading to formation of polyaromatic hydrocarbons, there is no quantitative, high temperature data on their reactions.

We report here rate constant determinations of displacement reactions of H atom on unsaturated hydrocarbons (acetylene, ethylene and benzene) with phenyl radical in a temperature range of 850-1300K, using very low pressure pyrolysis technique<sup>(1)</sup>. We have used nitrosobenzene as a thermal source of phenyl radicals. The unsaturated hydrocarbon and nitrosobenzene were admitted into a quartz Knudsen cell, where they rapidly mix and react. As an example, for acetylene as follows:



The flow of stable products and reactants out of the reactor was monitored by a quadrupole mass spectrometer and calibrated against known flow rates of these substances. Concentrations of the unsaturated reactant and stable products were calculated from corresponding flows, temperature and physical parameters of the reactor<sup>(2)</sup>. In the case of reaction of phenyl radicals with benzene, <sup>13</sup>C isotopically substituted benzene, was used in order to differentiate the biphenyl produced by the recombination reaction of phenyl radicals and the displacement reaction.

The following expression was used to obtain the rate of H atom displacement relative to the recombination rate to produce biphenyl.

$$\frac{k_{\text{dis}}}{k_{\text{rec}}^{1/2}} = \frac{\text{flow}(\text{C}_2\text{H}_2)}{[\text{C}_2\text{H}_2](\text{reactor volume} \times \text{flow}(\text{C}_6\text{H}_5)_2)^{1/2}} \quad (\text{for acetylene})$$

$$\begin{aligned} \frac{k_{\text{dis}}}{k_{\text{rec}}^{1/2}} &= (2.6 \pm 0.4) \times 10^3 (1 \text{ mole}^{-1}\text{sec}^{-1})^{1/2} \text{ for acetylene at 1000 K} \\ &= (2.1 \pm 0.3) \times 10^3 (1 \text{ mole}^{-1}\text{sec}^{-1})^{1/2} \text{ for ethylene at 1000 K} \\ &= (1.4 \pm 0.2) \times 10^3 (1 \text{ mole}^{-1}\text{sec}^{-1})^{1/2} \text{ for benzene at 1000 K} \end{aligned}$$

If we use estimated  $k_{\text{rec}} = 10^{9.5 \pm .5}$  (3) then,

$$k_{\text{dis}}(\text{C}_6\text{H}_5\cdot + \text{C}_2\text{H}_2) = 1.5 \times 10^8 \text{ l mole}^{-1}\text{sec}^{-1}$$

$$k_{\text{dis}}(\text{C}_6\text{H}_4\cdot + \text{C}_2\text{H}_4) = 1.2 \times 10^8 \text{ l mole}^{-1}\text{sec}^{-1}$$

$$k_{\text{dis}} (\text{C}_6\text{H}_5^\cdot + {}^{13}\text{C}_6\text{H}_6 = 7.7 \times 10^7 \text{ l mole}^{-1}\text{sec}^{-1})$$

A rate constant of  $4.5 \times 10^5 \text{ mole}^{-1}\text{sec}^{-1}$  for reaction of phenyl radical with benzene, at room temperature, has been measured <sup>(4)</sup>. Using this value and our high temperature results, for this reaction following Arrhenius parameters have been obtained

$$A = 10^{8.8} \text{ mole}^{-1}\text{sec}^{-1} \text{ and } E_a = 4.2 \text{ kcal mole}^{-1}$$

#### References

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- (2) David A. Robaugh and Stephen E. Stein, *Internat. J. Chem. Kinetics* 13, 445 (1981).
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Work supported by the Gas Research Institute.

**MEASUREMENT OF THE FRACTIONAL YIELD OF METHOXY  
FROM THE REACTION F PLUS METHANOL BY LASER INDUCED FLUORESCENCE  
AND CHEMILUMINESCENCE**

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The reaction of F atoms with methanol has been studied in a discharge flow reactor at 2 Torr and 298 K. Hydrogen abstraction occurred from the C-H bond giving hydroxymethyl and from the O-H bond giving methoxy, which was monitored by laser induced fluorescence (LIF). The concentration of F was measured by chemiluminescent titration with  $\text{Cl}_2$ . Addition of  $\text{F}_2$  downstream of the atom inlet, results in occurrence of the reaction,



In the presence of large excesses of methanol and  $\text{F}_2$ , the F atom regenerated by reaction (1) will attack another methanol leading to methoxy, or to repeated cycles of the chain until methoxy is formed. Using this procedure and LIF, we measured the fractional yield of methoxy from the primary reaction as  $0.40 \pm 0.15$ . There was no significant deuterium isotope effect at either C-H or O-H bonds. A visible chemiluminescence (CL) spectrum of the system showed high vibrational overtones of HF. The intensity of HF (4-0) showed a very sharp maximum at the stoichiometric endpoint, i.e. when all of the initial F and methanol were consumed. In the absence of added  $\text{F}_2$ , this occurred at 4 F atoms per methanol molecule. In the presence of  $\text{F}_2$ , the point of maximum intensity, and the endpoint stoichiometry, were altered by the occurrence of reaction (1). CL measurements, taken in this way, gave  $0.73 \pm 0.10$  as the fractional yield of methoxy from the primary reaction. The reliability and implications of these results will be discussed.

"Multiphoton Ionization Spectra of Radical Products in the  
 $F(^2P) + \text{Ketene System: } CH_2F, CH \text{ and } CF."$

by

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We have studied the reaction of  $F(^2P) + \text{Ketene}$  and  $F(^2P) + \text{Ketene-d}_2$  in a flow reactor and used resonance enhanced multiphoton ionization (REMPI) mass spectrometry to characterize the reaction products. The flow tube was operated at 2 torr total pressure with a 1000 cm/sec flow rate. The radicals,  $CH_2F$ ,  $CD_2F$ ,  $CH$  and  $CF$  were observed between wavelengths of 270-330 nm. The fluoromethyl radicals were identified as the nascent products of the reaction of fluorine with ketene.  $CH$  radicals (observed at 311 nm) were generated by the multi-step photolysis of ketene. The production mechanism that generated the  $CF$  radicals (observed between 344-358 nm) was not determined. This paper shows the usefulness of multiphoton ionization spectroscopy as a general detection technique in flow reactor studies. The study was also first to detect the observed free radicals by REMPI spectroscopy.

# AUTHOR INDEX

Adams, B. R.	164	Cohen, N.	66
Adams, G. F.	52	Colkett, M. B.	78
Adams, N.	133	Colussi, A. J.	20
Ahrens, A. F.	137	Come, G-M.	64
Anderson, J. G.	156	Cooper, R.	128
Anderson, S. M.	153	Craig, B. B.	142
Anner, O.	81	Crosley, D. R.	147
Arnett, E. M.	28	Curtis, R. A.	49
Asaba, T.	47	Cvetanovic, R. J.	71
Astalos, R. J.	159	Davis, M. J.	61
Atherton, S. J.	142	Deakyné, C. A.	136
Ausloos, P.	141	Dean, A. M.	97
Austin, J. W.	59	Denning, R. J.	79
Avila, I.	89	Dunning, T. H.	41, 45, 46
Ayscough, P. B.	65	Dodd, J. A.	37
Babcock, L.	96	Dolbier, W. R.	70
Baer, T.	31	Dominquez, R. M.	89, 90
Bagnall, G. N.	88	Dorey, R. C.	83
Balla, R. J.	154, 168	Dorko, E. A.	113
Barker, J. R.	35, 120, 121	Dulcey, C. S.	181
Barronnet, F.	63	Duray, J. P.	113
Batt, L.	74	Dijks, J. H. M.	69
Bauer, S. H.	118	Eades, R. A.	45, 46
Baulch, D. L.	65	Espenson, J. H.	39
Beck, K. M.	124	Estes, R. D.	85
Benson, S. W.	25	Fahr, A.	178
Berman, M. R.	115	Farrar, J. M.	49
Bhaskaran, K. A.	174	Fendel, J.	177
Brinkley, J. S.	52	Flynn, G. W.	107
Birks, J. W.	91	Foon, R.	79
Bogan, D. J.	122, 180, 181	Forst, W.	105
Bosco, S. R.	83	Fotakis, C.	123
Bowers, M. T.	110	Frank, P.	174
Brauer, B.E.	180	Freedman, A.	160
Brauman, J. I.	37	Frenklach, M.	62
Brezinsky, K.	157	Frey, H. M.	33
Brouard, M.	98	Fritz, B.	58
Brower, L.	144	Furue, H.	54
Brown, T. C.	23	Gajewski, J. J.	32
Brown, N. J.	108	Gardiner, W. C.	53
Brown, T. H.	120, 121	Gascon, F. G.	68
Brown, R. L.	131	Gilbert, K. E.	32
Brune, W. H.	158	Gilbert, R. G.	106
Brunning, J.	162	Glassman, I.	157
Carper, W. R.	83	Glessner, J. W.	113
Caballero, J.	113	Glicker, S.	165
Chattopadhyay, C.	142	Glinski, R. J.	91
Chen, F-T.	67	Golden, D. M.	143, 144
Chenier, J. H. B.	38	Gonzalez-Lopez, A.	68
Chinnick, G.	65	Gordon, R. J.	124
Chowdhury, P. K.	84	Green, N. J. B.	59
Chu, A-L.	116	Greenberg, A.	70
Chuchani, G.	89, 90	Greenblatt, G. D.	118
		Grela, M. A.	20

Grotheer, H. H.	172	Lin, M. C.	76
Gutman, D.	57	Litzinger, T. A.	157
Haas, Y.	81	Lorenz, K.	58
Halstead, J. A.	116	Louw, R.	69
Holloway, J. S.	117	Mallard, W. G.	178
Han, C-C.	37	Manion, J. A.	69
Hand, C. W.	180	Manka, M. J.	131
Harding, L. B.	50	Manuccia, T. J.	119
Hase, W. L.	29	Manzanares, E. R.	139
Heicklen, J.	168	Martin, I.	90
Heidner, R. F.	117	Matsui, H.	47
Heinemann, P.	150	Matula, R. A.	62
Helvajian, H.	117	McDonald, J. R.	112, 119,
Henchman, M.	96, 137		154
Herd, C.	96	McFadden, D. L.	163
Herron, J. T.	103	Meier, U.	172
Heydtmann, H.	177	Melius, C. F.	52
Hierl, P. M.	137	Meot-Ner (Mautner), M.	55, 134,
Howard, J. A.	38		135, 136
Hoyermann, K.	150	Mialocq, J-C.	101
Hudgens, J. W.	181	Michael, J. V.	146
Hule, R. E.	126	Miller, D. L.	62
Husain, D.	167	Mirodatos, C.	132
Hwang, J-T.	67	Mittal, L. J.	130
Hynes, A. J.	161	Mittal, J. P.	84, 130
Jackson, W. M.	169	Miyazaki, T.	56
Jasinski, J. M.	85	Morris, R. A.	163
Jeffries, J. B.	147	Mozurkewich, M.	95
Jolly, G. S.	156	Mulder, P.	69
Just, T.	172, 174	Muller, C.	64
Kajkowski, K. A.	87	Murphy, R. D.	83
Kamiya, K.	47	Nelson, H. H.	154
Kaufman, F.	40, 155	Nesbitt, F. L.	99
Kaufman, M. J.	180	Neta, P.	126
Kaye, J. A.	51	Nishi, N.	127
Kemper, P. R.	110	Nguyen, D.	128
Kern, R. D.	77	Nguyen, T. T.	23
King, D. S.	109	Okabe, H.	165
King, K. D.	23	O'Keefe, A.	112
Klein, F. S.	155	O'Neal, H. E.	18
Klemm, R. B.	99, 146	Ouellette, P.	92
Koeppel, G. W.	44	Pacey, P. D.	54
Koffend, J. B.	117	Pamidimukkala, K. M.	77
Kolb, C. E.	173	Papagiannakopoulos, P.	123
Kurylo, M. J.	92	Paraskevopoulos, G.	156
Lamb, J. J.	25	Paulson, J. F.	96, 137,
Lee, E. K. C.	94, 164		140
Lee, L. C.	139	Pellett, G. L.	166
Lengsfeld, B. H.	52	Pilling, M. J.	59, 98
Li, X.	169	Plane, J. M. C.	167
Lias, S. G.	141	Preidel, M.	58
Liebman, J. F.	70	Rabinowitz, M. J.	53
Lightfoot, P. D.	98	Rama Rao, K. V. S.	84
Lim, K.	106	Rashed, O.	108
Lin, C-Y.	76	Ravishankara, A. R.	161



Reeves, R. R.	116	Vogin, B.	63
Rnasa, D.	58	Wagner, A. F.	50, 61
Rickborn, S. F.	18	Walsh, R.	19
Riekert, G.	172	Wang, H-t.	122, 180
Ring, M. A.	18	Washida, N.	127, 149
Ritchey, C. M.	113	Weston, R. E.	73, 107
Robaugh, D.	148	Whitefield, P. D.	115
Rogers, D. S.	18	Wiessenfeld, J. R.	118
Roscoe, J. M.	152	Wine, P. H.	161
Rossi, M. J.	143, 144	Woodin, R. L.	87
Rotinov, A.	89, 90	Wolfrum, J.	42
Ruhman, S.	81	Woprmhoudt, J.	160
Rumack, D.	134	Xiang, C. C.	167
Sanders, W. A.	122, 180	Zellner, R.	58
Sato, S.	153	Zellweger, J-M.	120, 121
Sayah, N.	169	Zirrolli, J. A.	83
Scacchi, G.	63, 64		
Schaefer, H. F.	26		
Seaver, M.	119		
Selamoglu, N.	143		
Sherwell, J.	128		
Shinohara, H.	127		
Sidebottom, H. W.	88		
Sieck, L. W.	138		
Silver, J. A.	173		
Singleton, D. I.	156		
Slagle, I. R.	57		
Smalley, J. F.	99		
Smith, G. P.	147		
Sonnenfroh, D. M.	49		
Srinivasan, C.	129		
Stanton, A. C.	160		
Stein, S. E.	22, 131, 178		
Stephenson, J. C.	36, 101, 109		
Stief, L. J.	162		
Stone, B. M.	164		
Subramaniam, P.	129		
Sugiyama, K.	153		
Sutherland, J. W.	146		
Suto, M.	139		
Sverdlik, D. I.	44		
Swanson, J. F.	83		
Tardieu de Maleissye, J.	48		
Tedder, J. M.	111		
Tooney, D. W.	158		
Troe, J.	27		
Trolter, M.	118		
Tsang, W.	80, 148		
Tso, T-L.	94		
Tsunashima, S.	153		
Umemoto, H.	153		
Viggiano, A. A.	95, 137, 140		

END

8-87

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